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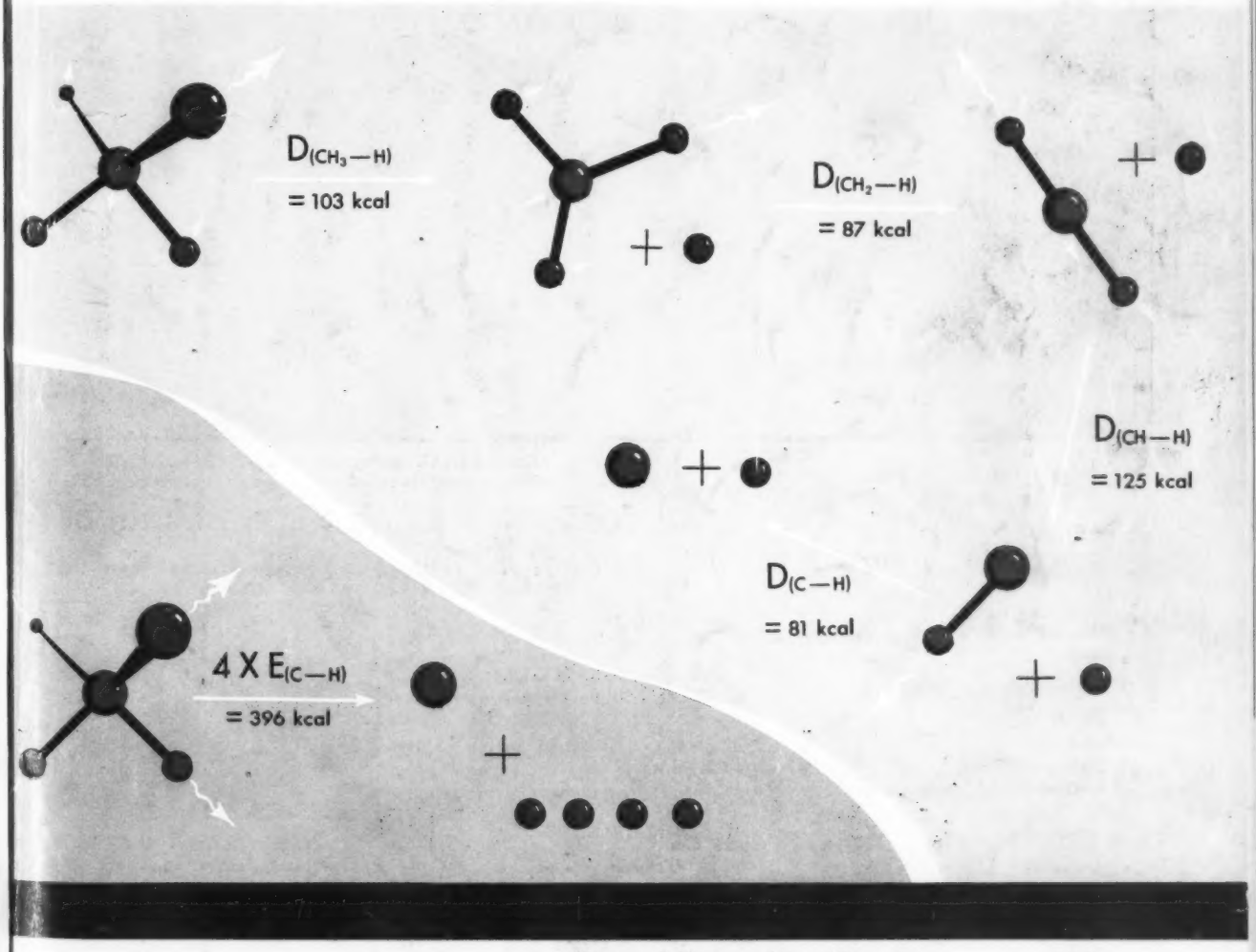


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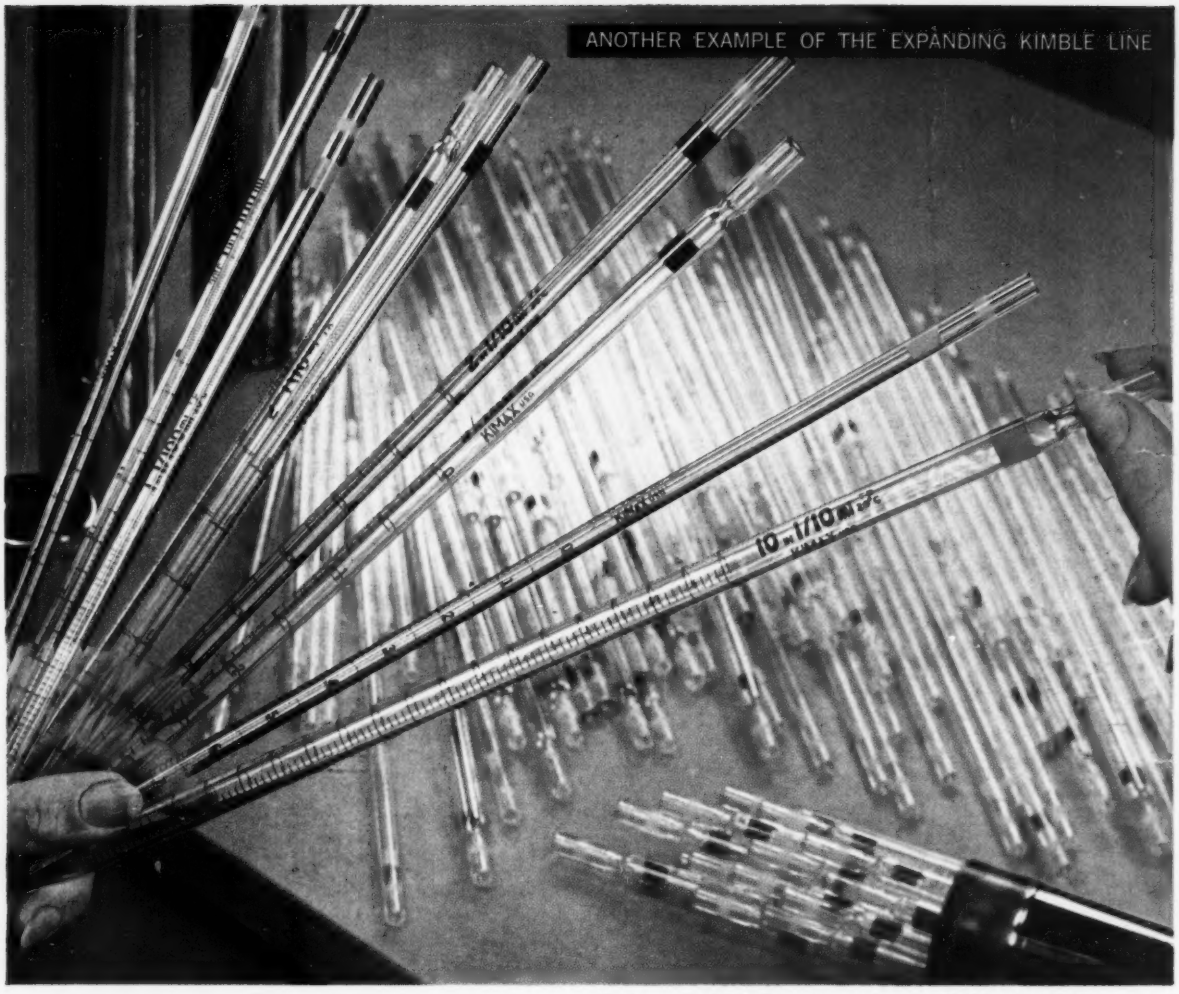


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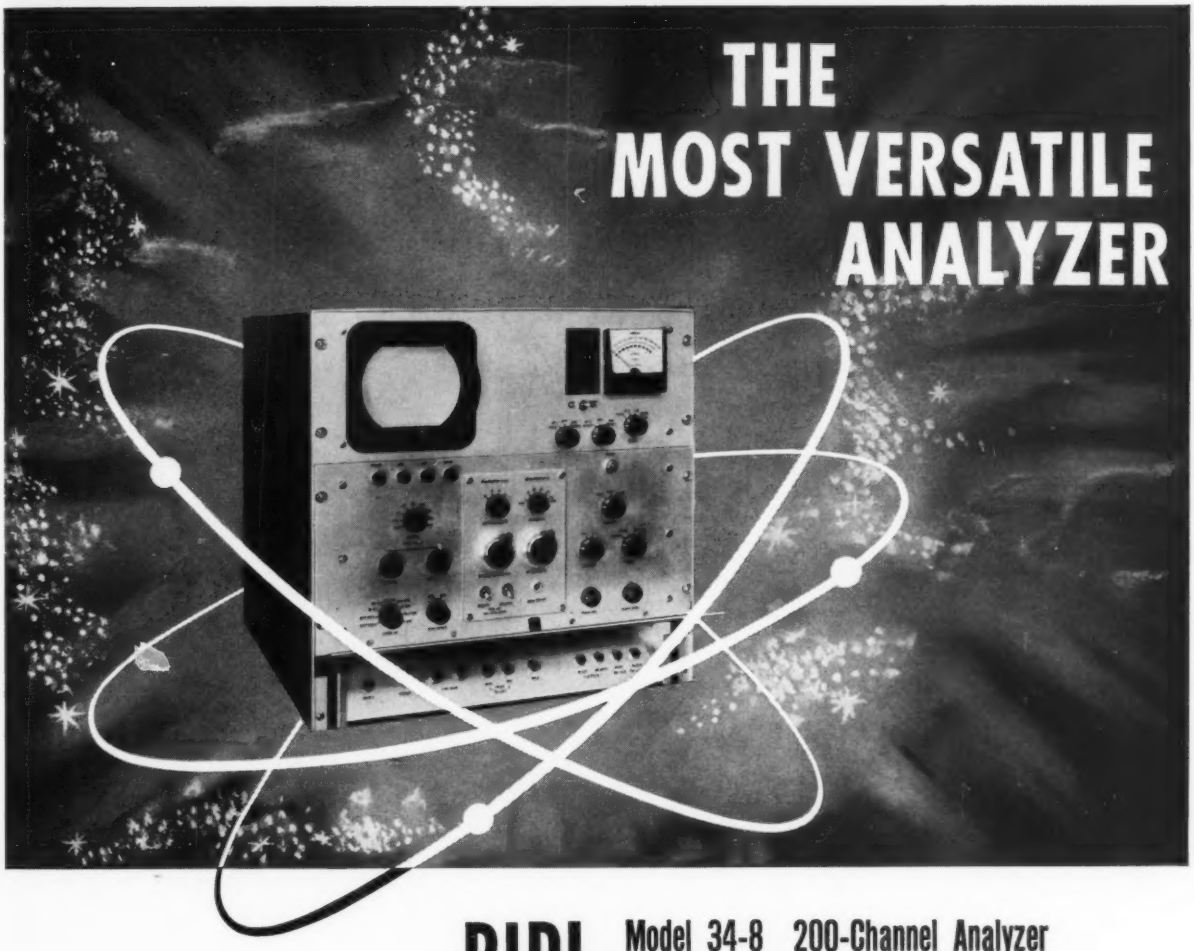


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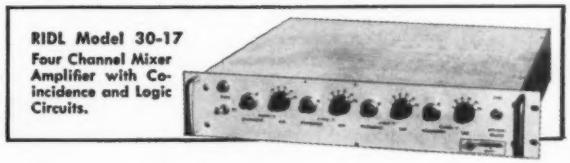

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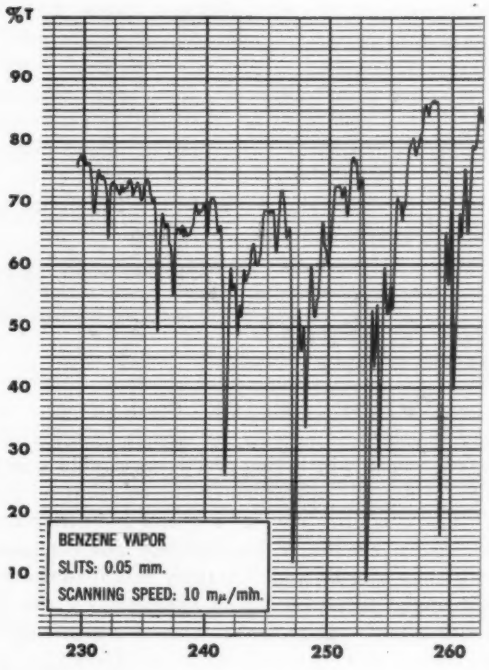


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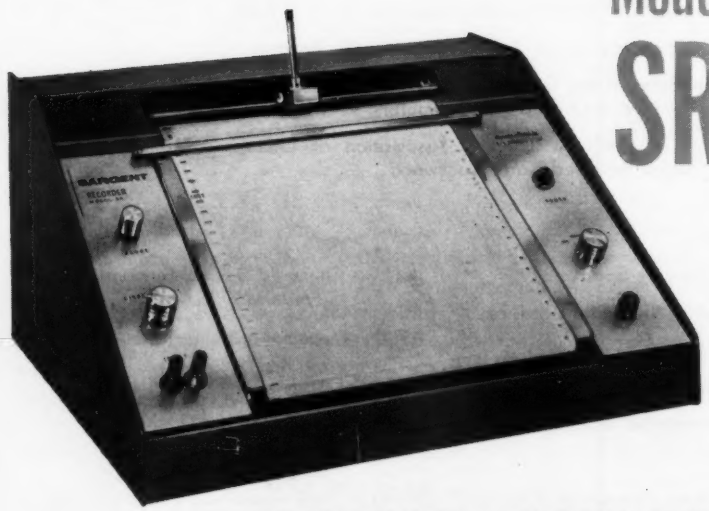


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# Chemical Instrumentation

**S. Z. LEWIN,** New York University, Washington Square, New York 3, N. Y.

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*This series of articles presents a survey of the basic principles, characteristics, and limitations of those instruments which find important applications in chemical work. The emphasis is on commercially available equipment, and approximate prices are quoted to show the order of magnitude of cost of the various types of design and construction.*

## 13. Nuclear Radiation Electronic Gear (Continued)

Few fields of instrumentation are as well endowed with commercial firms producing a wide variety of models for all types of use as is the nuclear field. This is in large part due to the subsidization of engineering developments in this field by the federal government because of its interest in fissionable materials. The instrument user is the fortunate beneficiary of this situation, for he now has available a wide range of instruments from which to choose the specific ones that are best suited to his needs and budget.

The following paragraphs summarize the types of instrumentation currently available from the major U.S. manufacturers. Since in many cases equivalent models of instruments are produced by several manufacturers, not all the models of each supplier are mentioned in detail. Also, the design of nuclear detection instrumentation has developed rapidly in the past decade, and model changes have taken place with greater frequency in this field than in most other areas of instrumentation. This summary emphasizes the most recent models of the various manufacturers.

### Lionel/Anton Electronic Laboratories

One of the principal suppliers of nuclear detector tubes, and a manufacturer of a line of radiological survey and counting equipment, is Lionel Electronic Laboratories, Brooklyn 37, New York, formerly known as Anton Electronic Laboratories. This company's detector tubes have been mentioned earlier in this series (*cf.* No. 12, "Nuclear Radiation Detectors"), and include a wide range of sizes and shapes, ranging from a 0.1-inch diameter thin-wall beta-gamma dipping or probe tube to cosmic ray and neutron detectors several feet long and several inches in diameter. A useful and unique feature of this line is a number of "pancake"-shaped detectors that are sensitive to alphas and betas, but relatively insensitive to gammas, which mostly pass through the thin, flat detector without producing ionizing events. This manufacturer specializes in the production of halogen-quenched Geiger-Mueller detectors, which have the advantage of very long life (not limited by total number of counts recorded, as is the case with organic vapor-quenched G.M.-tubes), and the ability to withstand high overvoltages.

A portable, transistorized survey meter recently introduced by this manufacturer is shown in Figure 27. This instrument (Model 701, $139.50 with beta-gamma probe only; $225 with additional mica end-window probe) is powered by five 1.5-volt flashlight batteries which are contained in a removable compartment at the bottom of the instrument, as shown in Figure 28. The high voltage (930 ± 20 v) for the G.M.-tube is obtained by means of a transistor oscillator, and is regulated by a corona discharge voltage-regulator tube. The read-out is aural *via* the head-set, or visual *via* a count-rate meter. The ranges of this instrument are calibrated for 0–0.5, 0–5, and 0–50 milliroentgens per hour, which are equivalent (for a radium source) to 0–300, 0–3000, and 0–30,000 counts per minute. A calibrated Ra D and E source is imbedded in the wall of the instrument case, and the meter scales can be standardized simply by placing the probe next to this check source and making appropriate adjustment of a variable resistor.

**Figure 27. Model 701 Alpha-beta-gamma survey meter of Lionel/Anton Electronic Labs. The beta-gamma probe is shown plugged in to the measuring circuitry. It consists of a thin-wall halogen-quenched Geiger-Mueller tube. The alpha-beta detector shown beside the instrument has a mica end-window.**

A more precise measuring instrument is the Model 45 Radioactivity Scaler-Ratemeter ($495), the electronic design of which is illustrated in Figure 29. An amplifier-discriminator circuit shapes the detector pulses, and passes only those the amplitudes of which are above a minimum value, which may be chosen by means of an internal control. The pulses may be fed either to a rate-meter circuit that converts them into a meter reading whose deflection is proportional to the counting rate, or to a scaler circuit that registers the total count detected in a given time interval. An audio circuit is provided for producing a loud click for each pulse. The power supply circuitry provides both regulated and unregulated supply voltages for the other circuits. Because of the versatility of the read-out, this instrument is useful for lecture demonstration purposes, as well

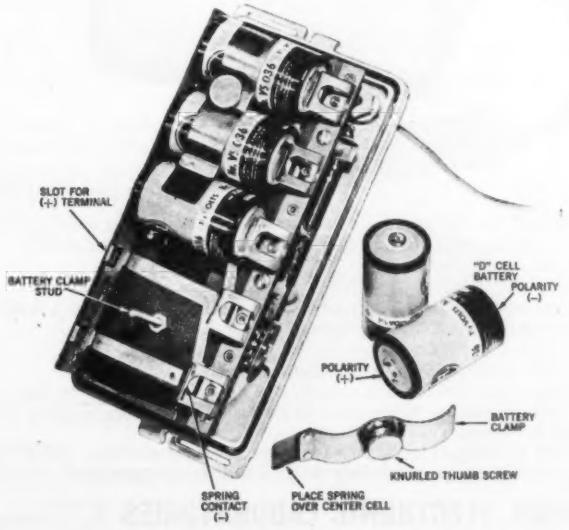


**Figure 28. Battery section of Lionel/Anton portable survey meter.**

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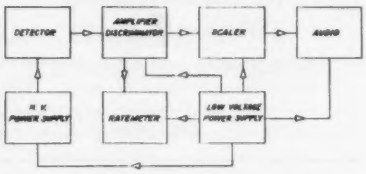


**Figure 29. Block diagram of electronics of Model 45 Radioactivity Scaler-Ratemeter of Lionel/Anton Electronic Laboratories.**

(i.e., pulses separated by 200 microseconds or more are detected as individual counts).

### Tracerlab

One of the most extensive lines of detectors and counting systems in the nuclear field is available from Tracerlab, Inc., Waltham 54, Massachusetts. This company, which was among the first to produce commercial radiological instrumentation during and after World War II, offers not only instruments, but also labeled compounds, radioactive sources, decontamination services, and other supplies and services.

An example of this manufacturer's survey instruments is the Model SU-14 Alpha Beta Gamma Survey Meter ($260), the circuitry of which is shown in Figure 30. The lower portion of the diagram shows the power supply section, which is based upon four 1.5-volt flashlight batteries, and three 45-volt portable-radio type batteries. A relaxation oscillator, consisting of *V-1*, *R-1*, and *C-1* feeds pulses of a sawtooth waveform through a pulse sharpening network, *R-2* and *C-2*, to the grid of *V-3*. The subsequent pulses of plate current through *T-1* produce large ac voltage pulses which are rectified by *V-4* and filtered by the *R-C* filter. A dc voltage at *V-5* causes a corona discharge to occur, and this current flows through *R-13*. Any small changes in this corona regulation current through *R-13* caused by battery decay of *B-1* and *B-2* will affect the bias voltage on the grid of *V-2*. The plate voltage of *V-2* will increase if its grid voltage decreases. The bias voltage on *V-3* is therefore increased as the regulator current through *R-13* drops. With an increase in bias, *V-3* will draw a large pulse current through *T-1*, thereby increasing the voltage level at the corona regulator tube.

The upper portion of Figure 30 shows the ratemeter circuit. Tube *V-7* is the normally-on tube of a univibrator circuit. Since its plate voltage and grid-bias are derived from a regulated supply voltage, the ratemeter sensitivity is constant, independent of battery age or condition over a considerable range. The ranges of this instrument are 0–0.25, 0–2.5, and 0–25 mr/hr. The accuracy is ±15% of the mr/hr scales for Co-60 radiation.

Tracerlab produces a number of other


(*Continued on page A392*)

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survey instruments, including pocket dosimeters, ionization chamber survey meters, and laboratory monitors. This company also manufactures a variety of scalers and ratemeters, comprising examples of most of the types of read-out. These include binary scalers, decimal scalers, glow transfer tube decade scalers, and automatic data print-out devices. Some idea of the characteristics of the several types of scalers available can be gained from the data in Table 1, p. A404.

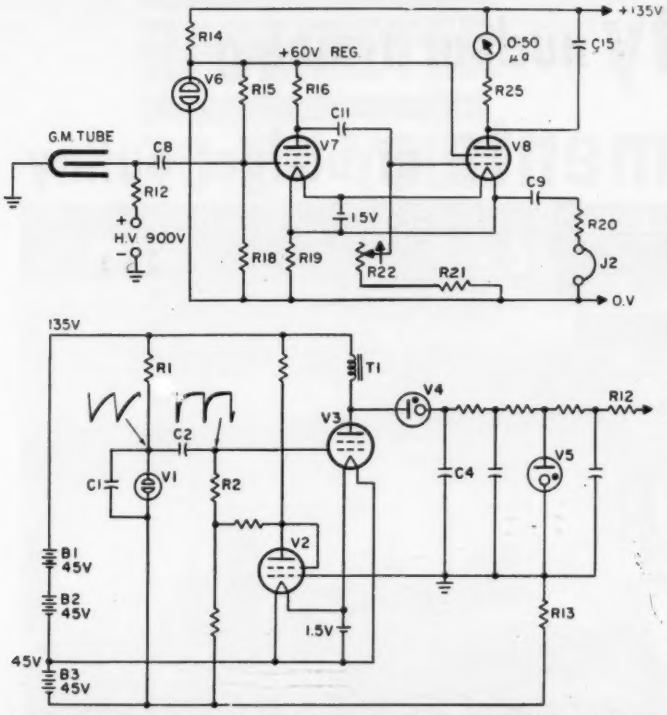


Figure 30. Schematic of the electronic circuitry of the Tracerlab Model SU-14 Survey Meter.

One of the more recent radiation detection systems developed by Tracerlab is the Omni/Guard Low Background Beta Counting System ($4390 to $7980, depending on accessories). The principles of the design of this system are illustrated by the block diagram shown in Figure 31. The sample is positioned close (within 1 mm) to the window of an ultra-thin end-window (less than 125 microgram/cm²) gas flow counter. This detector yields pulses due to the sample, together with pulses due to cosmic radiation, and surrounding terrestrial radiation. A dome-shaped gas flow counter surrounds the sample counter, enclosing all but the window of the latter. The pulses from the guard counter are compared with those from the sample counter by means of the anti-coincidence unit. Cosmic radiation and energetic terrestrial radiation will cause simultaneous ionizations to occur in both the guard and sample counters, and such coincidences will not be counted. Only pulses originating in the sample counter, and which do not coincide with pulses occurring in the guard counter, are passed by the anti-coincidence unit. Thus, the scaler can be set to count only the sample, free of most of the background

(*Continued on page A396*)

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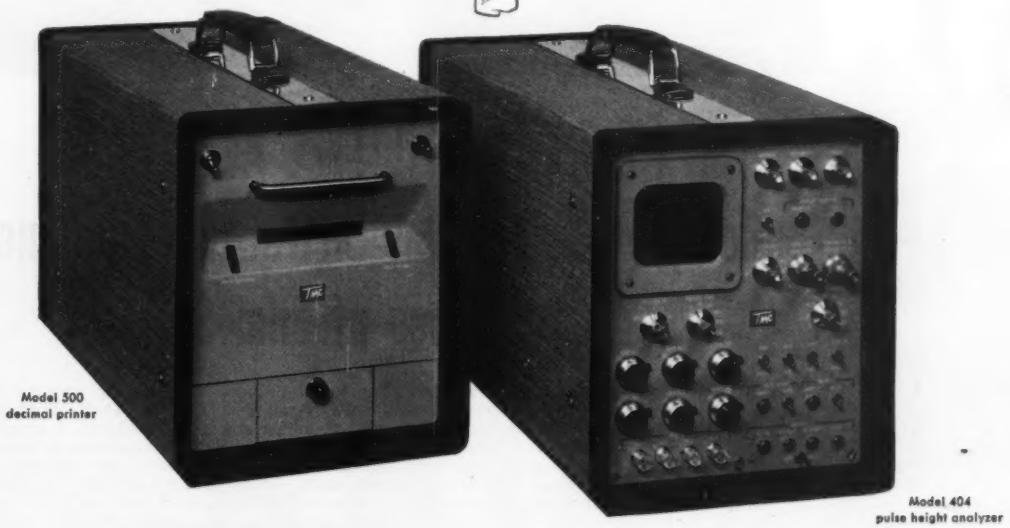

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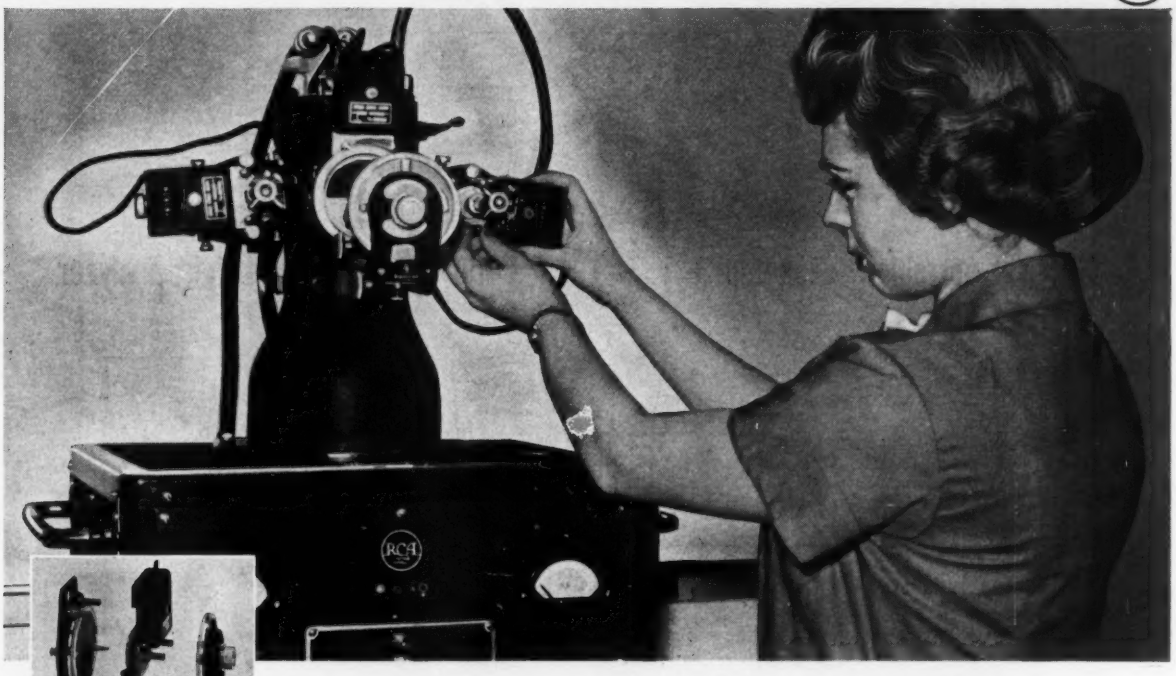

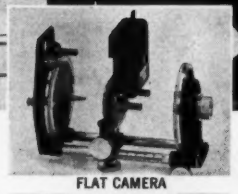

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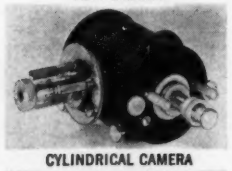

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pulses. As the Figure shows, the scaler may also be used to count directly the cosmic ray background, as well as the sample plus its background.

ing of large numbers of samples on a routine basis is the Multi/Matic sample changer ($1440), shown in schematic diagram in Figure 32. Samples are automatically elevated to the counting position, counted for the desired period, then removed and a new sample placed

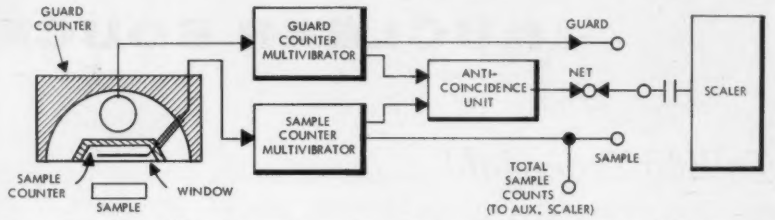



**Figure 31. The Omni/Guard Low Background Beta Counting System of Tracerlab in block diagram.**

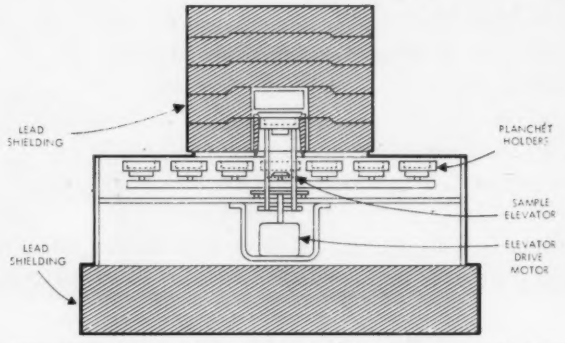
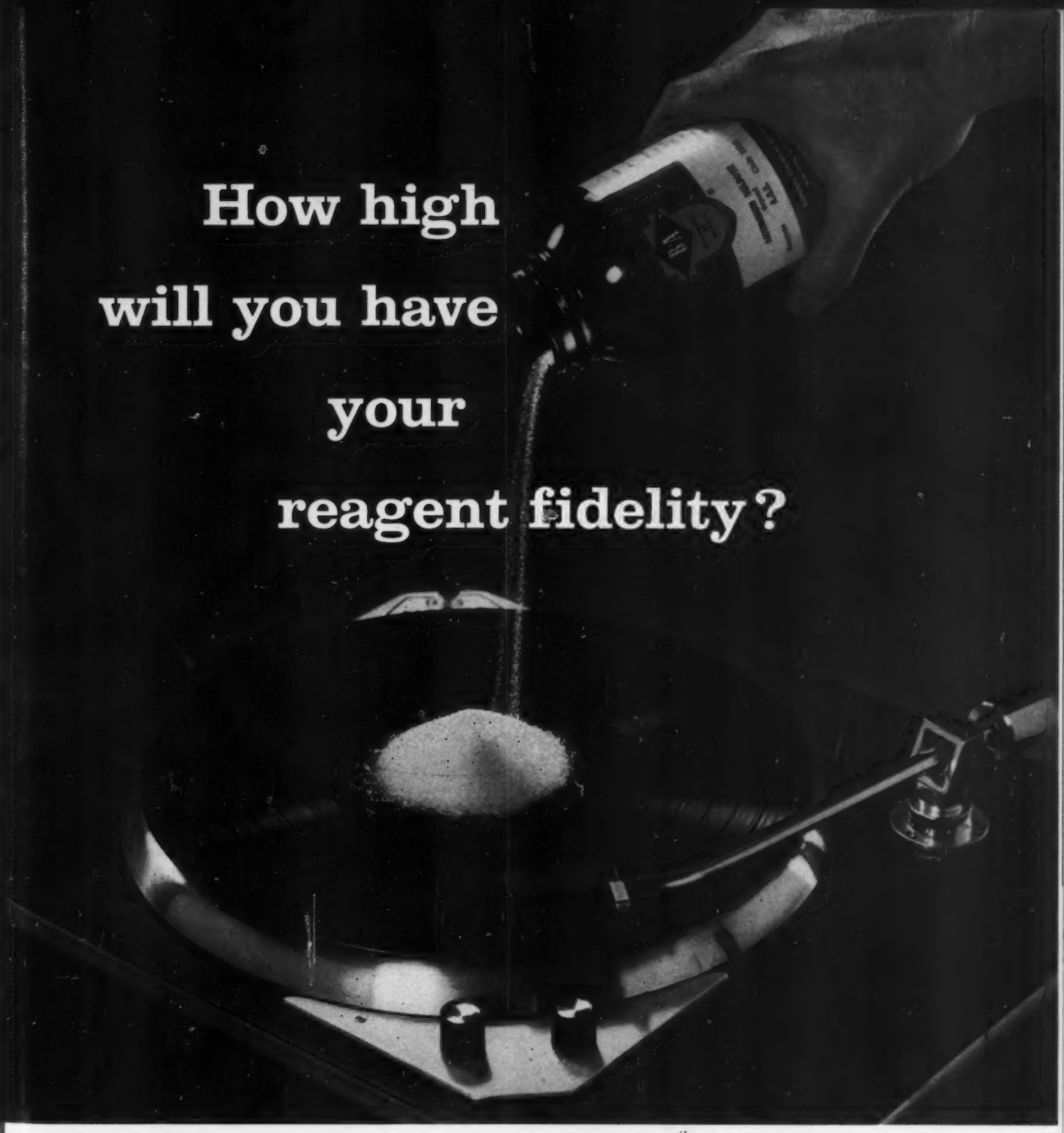



**Figure 32. Diagram of the design of the Tracerlab Multi/Matic automatic sample changer.**

A convenient accessory for the count- *(Continued on page A402)*




To be considered truly hi-fi, an amplifier's distortion at rated output must not exceed 1% at 20 CPS and 20,000 CPS. B&A reagents meet standards far higher than these. Their maximum allowable impurities are limited to thousandths and ten thousandths of a percent.

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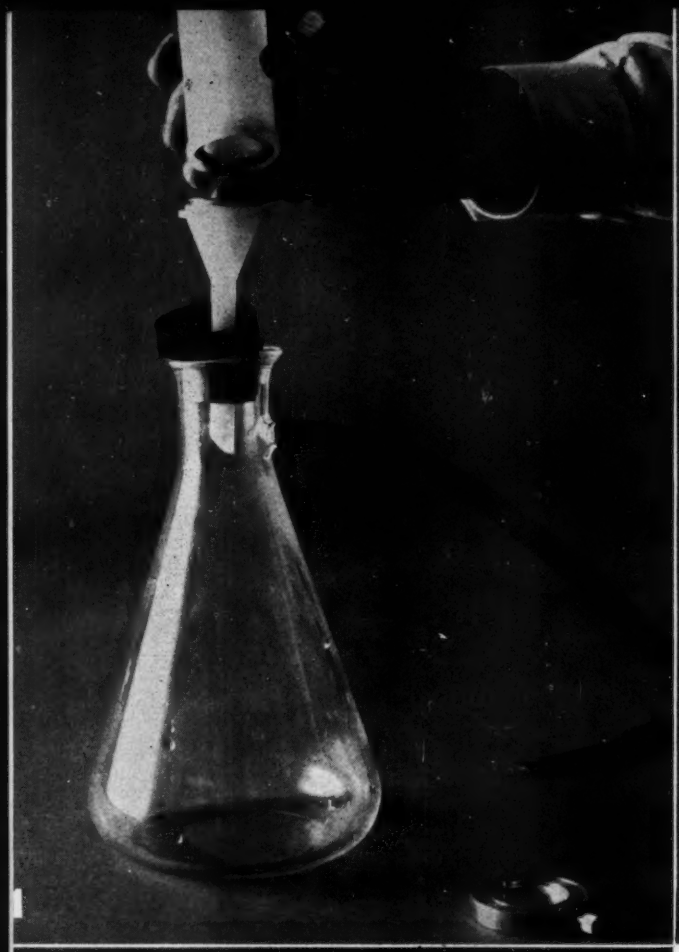

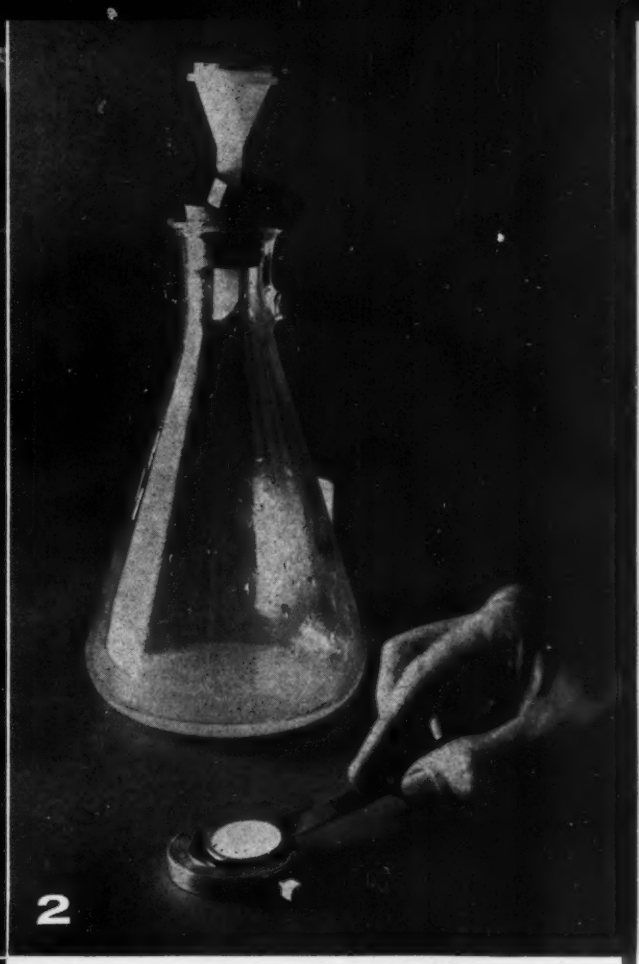

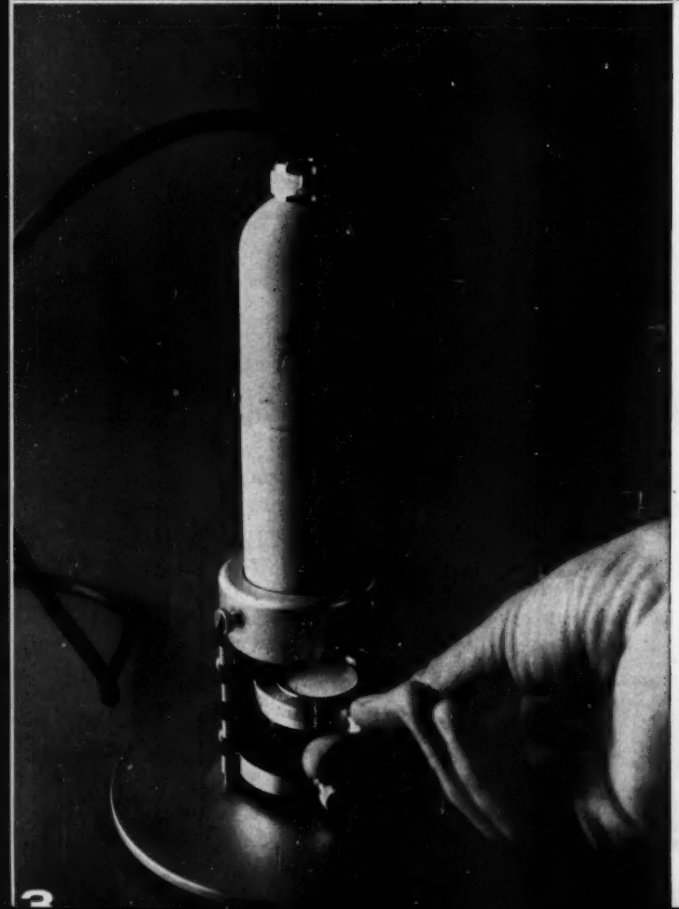

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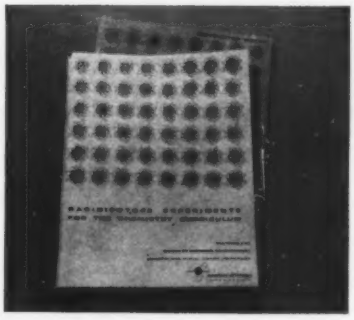

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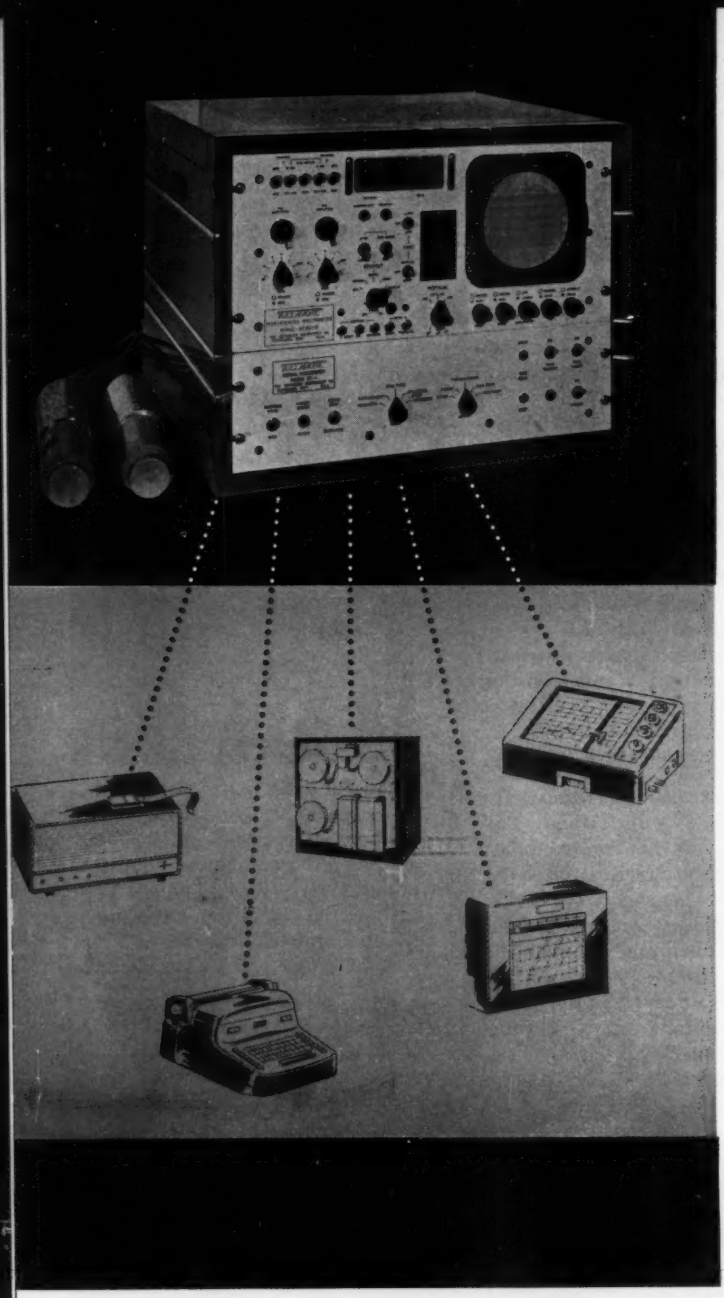

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Another approach to the counting of low-energy samples under conditions that lead to discrimination against the natural background is embodied in the Model LSC-10 Liquid Scintillation Counting System (semiautomatic $6500, fully automatic $9950). Figure 33 shows a block diagram of the electronic design of this system. The scintillator is in the form of a well, contained in a deep-freeze refrigeration unit. The samples are inserted into the well cavity, and produce scintillations, which are viewed by two photomultipliers mounted at 90° to each other. The deep freeze is used because the noise level of the photomultipliers is very much reduced if they are operated at reduced temperatures. The 90° mounting permits the two detectors to view the scintillator and to sense all light flashes produced by the sample, yet they do not view each other and do not sense the phosphorescence produced in each by natural background K-40 activity or by cosmic radiation.

The signals from the two phototubes are amplified, and passed by a lower level discriminator to a coincidence unit. The lower level discriminator passes only those

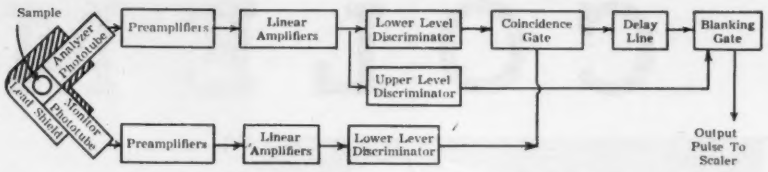


**Figure 33. Block diagram of electronic system of the Tracerlab Model LSC-10 liquid scintillation counting system.**

signals whose amplitude exceeds a given value, thus rejecting a portion of the spurious noise signals. The coincidence gate only passes those pulses which were simultaneous in both phototubes, providing additional discrimination against random noise signals. The upper level discriminator permits only those signals to pass which do not exceed in amplitude a given value, rejecting some more of the random noise signals. The discriminators also permit the output to be selected for some particular isotope in a mixture of isotopes, by choosing the upper and lower levels so as to pass the desired pulses, and to reject those from weaker or stronger radiations.

A sample changing device permits up to forty 20-ml vials to be mounted on a turntable and allows the operator to transfer a sample from the turntable into the counting cell without opening the freezer. This permits the system to remain dark-adapted throughout the series of measurements, and assures constant operating conditions for all samples.

A type of nuclear radiation instrumentation that has become increasingly important in recent years, as commercial models at reasonable prices have become available, is the radiological spectrometer. This instrument is based upon the pulse height analysis of the light flashes produced by nuclear radiations in a scintillator. Essentially, it consists of a scintillation detector, preamplifier, linear amplifier, lower level discriminator, upper level discriminator, and ratemeter or scaler circuitry for the detection of the output signals. A *single-channel spectrometer* has one combination of circuits, as described, and no memory circuit, so that the information is read out in a point-by-point fashion, for each setting of the discriminators.

Tracerlab manufactures a number of single channel spectrometers. Model SC-76 ($875) is simply a linear amplifier with lower and upper level discriminators. The amplifier rise time is 0.25 microsecond; a 250-fold overload can be accepted without overshoot or double pulsing; the maximum gain is 3000; and the input sensitivity is 2.0 millivolts. The lower discriminator limit is 5 volts, and

(*Continued on page A404*)

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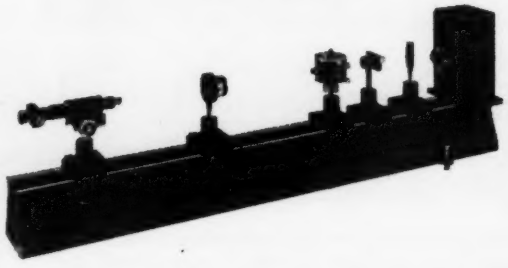

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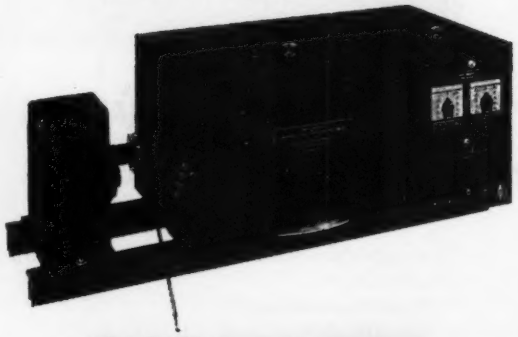

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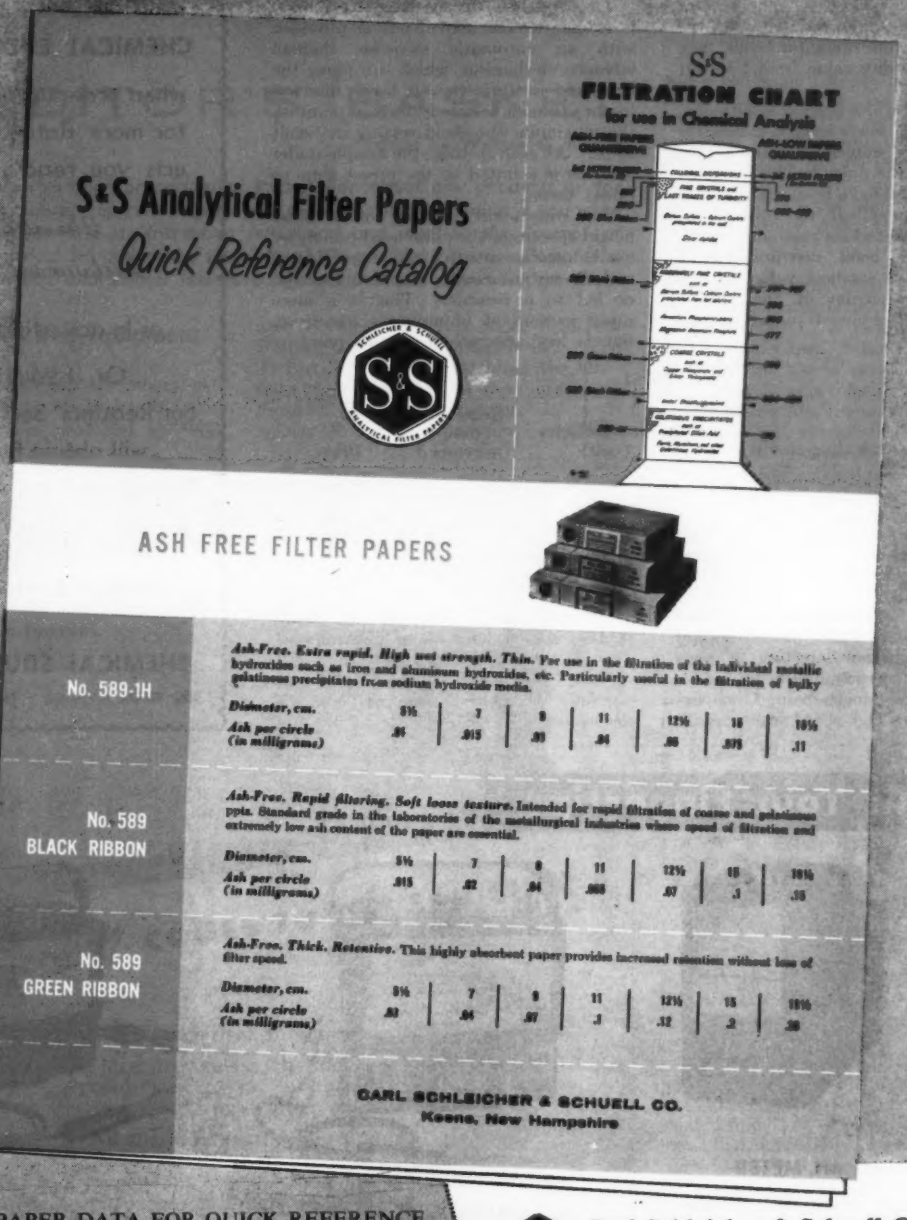
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the upper limit is 105 volts. The window width, i.e., the difference between the lower and upper discriminator levels, may be chosen to be any value from 1 to 101 volts.

If the window width is set at some value, say 1.0 v., and the lower level discriminator is set at various values from the lowest to the highest, the pulse height spectrum of the sample will have been scanned in a *differential* manner. If the upper level discriminator is set at its maximum value, and the lower level discriminator is scanned from the smallest value up, the pulse height spectrum of the sample will have been obtained in an *integral* manner.

preset or elapsed-time synchronous timer. It permits precision measurements of the pulse height spectrum by either the differential or the integral techniques.

The Model SC-78S spectrometer ($2600) is similar to the above, but is provided with an automatic stepwise channel advance mechanism, which can move the threshold setting (lower level discriminator) from a selected starting point to the maximum threshold setting in 1-volt steps. At each setting, the sample under analysis is counted to the preset time or preset count.

For continuous plotting of a pulse height spectrum, the pulse height analyzer can be combined with a ratemeter circuit, and the output can be observed visually, or fed to a recorder. This is a more rapid method of obtaining a spectrum, but is less accurate than the point-by

Table 1

| Model | Scaling circuit | Input sensitivity (volt) | Resolving time (microsec.) | Price |
|---|---|---|---|---|
| SC-70 | Beam-switching | 0.05–2.0 | 1 | $1575 |
| SC-33B[a] | Decade | 0.1 –0.5 | 1 | 795 |
| SC-19A | Binary | 0.25 | 7 - | 495 |
| SC-90 | Glow-transfer | 0.25 | <200 | 360 |

[a] No longer in production.

The Model SC-81 spectrometer ($1700) includes a high-voltage power supply (for the scintillation detector), a non-overloading linear amplifier, a pulse height analyzer (single-channel, as described above), a high-speed scaler, and a point procedure. The Model SC-80 ($1470) is such a ratemeter spectrometer.

*Next: Conclusion of the survey of commercially available nuclear radiation instrumentation.*

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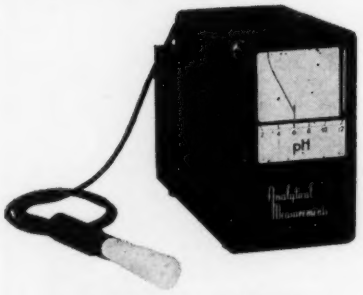
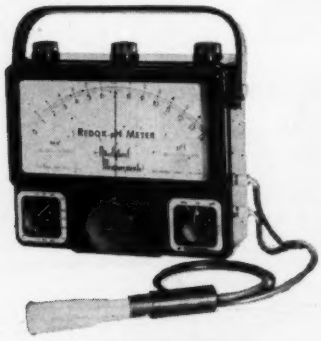
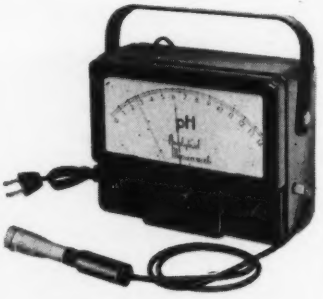


**RECORDING pH METER**
A pH meter and strip chart recorder in one. Line operated. Simple to operate. Continuously indicating. Write for Bulletin No. 3R.



**REDOX-pH METER**
Dual Probe. Line operated. Large 0-14 pH scale. For simultaneous millivolt and pH readings without changing electrodes. Temperature compensator 0-100°C.
Write for Bulletin No. 700 MV-pH.



**BIG SCALE pH METER**
Line operated with protected Analytical pH Probe Unit. Large 7" 0-14 pH scale One operating control.
Write for Bulletin No. 700.

**POCKET pH METER**
Battery operated. Completely self contained in water-proof everready case with shoulder strap. Meter scaled 2-12 pH, with simple adjustment for full pH scale.
Write for Bulletin No. 100.

**Prices of Analytical pH Meters start at $125.00.**

Analytical Measurements, Inc.
585 Main Street Chatham, New Jersey

Chem Ed

# *Out of the* EDITOR'S BASKET

*Edited by William G. Kessel*

***When writing for additional information about new products or for new literature, your inquiry will receive prompt attention if you write on your firm or institution letterhead and mention the Journal of Chemical Education and the date of the particular issue. Pamphlets, booklets and similar literature are gratis unless otherwise specified.***

## New Apparatus and Equipment

▶ A totally new concept in laboratory equipment has just been added to the line polyethylene labware produced by Pioneer Plastics, Inc., Box 8066, Arlington Branch, Jacksonville 11, Florida. The Twistcock Connector combines the functions of a Stopcock and a quick disconnect Flexible Tubing Connector. It seals against 40 lb water pressure. Available through leading supply houses or direct from the manufacturer.

▶ Labasco, laboratory equipment suppliers offer through their dealers a new laboratory burner, "Flexiflame," with several desirable innovations.

▶ Corner-Scope distillation rack offers a new concept in function and style for a laboratory distillation rack. Wasted corner space is utilized and two independent complex setups can be carried on simultaneously without crowding of equipment or personnel. Write Metalab Equipment Co., 270 Duffy Ave., Hicksville, L. I., New York, N. Y.

▶ A precision differential thermistor thermometer, capable of measuring temperatures to 0.001°C, is now available from Fiske Associates, Bethel, Connecticut. Designed for use in measuring temperature fluctuations in colorimetry, change-of-state experiments, research reaction studies, cryoscopy, chemical and medical research, these new precision thermometers open whole new areas of temperature measurement and calibration. They excel ordinary resistance thermometers in sensitivity, have lower heat capacity, and generally are smaller and more rugged.

▶ Waring Products Corp. of Winsted, Connecticut, a subsidiary of Dynamics Corp. of America, has announced the addition of a new model, LB-1, to their especially developed line of Blendors for commercial, medical, scientific, dietetic, and industrial use.

▶ Hudson Bay Co., Labline, 3070 W. Grand Ave., Chicago 22, Illinois, announces the addition of a 4-cubic foot upright chamber to its present line of temperature-humidity test cabinets. This high-performance unit has a temperature range of 0 to 200°F with a control tolerance of ±2°F and a humidity range of 20 to 95% RH within ±5%. Ask for *Bulletin No. 31.*

▶ California Scientific Glass Co., 9811 E. Rush St., El Monte, California, announces the availability of Orseal barosilicate glass joints. These Series 7700 do not require lubrication, are vacuum-tight and will withstand up to 50 lb internal pressure. They may be joined within 10 degrees of axial centers and secured with standard metal ball and socket clamp.

▶ A highly sensitive, fast responding electronic relay that will switch up to 15 amp with a 1.8 microamp or less control signal has just been marketed by Cenco as No. 99790 Electronic Switch. Write Central Scientific Co., 1700 Irving Park Rd, Chicago 13, Illinois.

▶ The Dipolemeter DM 01 is a precision measuring instrument designed for the evaluation of the molecular electrical dipole moment of liquids by accurate measurement of the dielectric constant. It further permits exact determinations of the dielectric constant of liquids, pastes, and solids for non-destructive quality control, purity test, dielectric analyses, chemical investigations, etc., because of its extremely sen-

*(Continued on page A407)*

*Beauty* COMES TO THE LAB SINK

*contact your*

**Laboratory Furniture Manufacturer**

*or write direct for Bulletin L8-R*

GONE, the drab brown—the dull black.

Here, in ageless chemical porcelain, cool "surf-green," soft "mist-gray" and sparkling white.

All made from the one material which requires no corrosion guide—no warning sign "don't put sulphuric and chromic acids here"—for these incomparable porcelain laboratory sinks will handle any corrosive, weak or strong, hot or cold—and without time limit.

Match the beauty of your new lab with the beauty of these impervious sinks, as permanent as the building in which they are installed.

*Chemical Ceramics Division*

U. S. STONEWARE

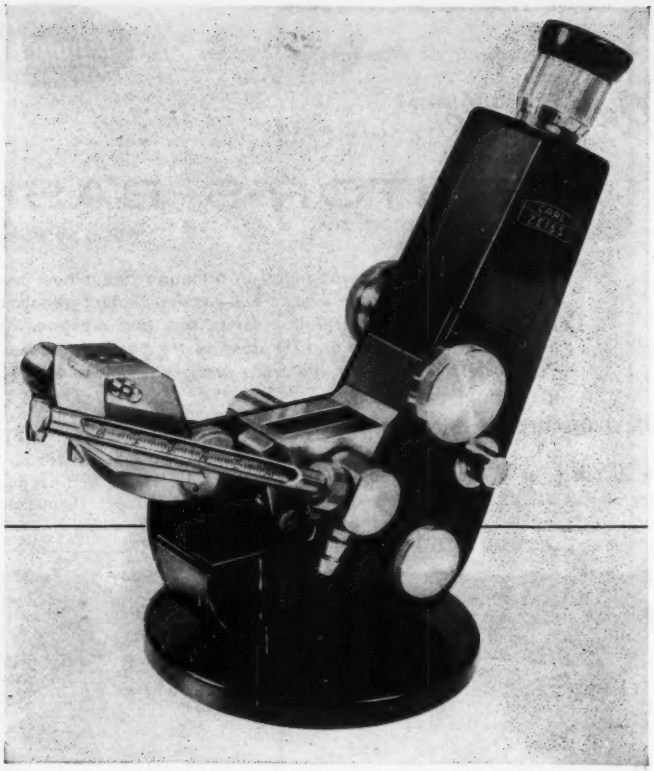
AKRON 9, OHIO

339-G

CARL ZEISS

WEST GERMANY

**For utmost ease and speed in checking liquids and solids**



# The famous ABBE REFRACTOMETER

### Incorporates the following features:

Range of measurements: $n_D$ 1.3 to $n_D$ 1.71 and sugar percentage scale 0% to 95%. For liquids and solids by transmitted and reflected light.

Measuring surface of index prism always at horizontal position.

Observation telescope mounted stationary at an inclined position to carry out measurements at a relaxed posture.

Border line of total reflection and scales are observed simultaneously in telescope.

Measuring prism in heating mount can be easily interchanged.

All movable parts are fully protected by being entirely enclosed within the housing.

Special index prism in heating mount available for measurements up to $n_D$ 1.85 (on special order only).

For highest-accuracy measurements, an Ultra-Thermostat with different constancy of temperature ±0.005° is available as an accessory.

In addition to the above model, the new Abbe Refractometer Model B is available for use where high temperatures are involved. This model is equipped with temperature controls, and finds a wide use in industrial laboratories.

*Write for free detailed literature*

**CARL ZEISS, INC.**

485 FIFTH AVENUE, NEW YORK 17, N. Y.

COMPLETE SERVICE FACILITIES

## *Out of the* EDITOR'S BASKET

sitive measuring range ($2.10^{-5}$ for liquids). Write the Kahl Scientific Instrument Corp., P.O. Box 1166, El Cajon (San Diego), California.

▶ Industrial Instruments, Inc., 89 Commerce Rd., Cedar Grove, Essex Co., New Jersey, offers a portable model OA-3 dissolved oxygen analyzer. The instrument utilizes the unique reactivity of metallic thallium to traces of oxygen producing thallons hydroxide which increases the conductivity of the water.

▶ A triple-service Fyr-Fyter All-Purpose Dry Chemical Fire Extinguisher, now available for built-in wall cabinet installation, greatly simplifies and speeds modern-day interior fire protection. The extinguisher, said to be the latest major development in the safety field, is Underwriters' and Factory Mutual approved for combatting "all" classes of fire; general combustible, burning liquid and electrical fires. Cabinet equipped with the All-Purpose extinguisher thus becomes a complete fire control center.

The Fyr-Fyter high capacity 20 lb All-Purpose extinguisher is sized for installation in the company's architecturally engineered series of Model 480 cabinets. Cabinets can be furnished in all standard dimensions or can be custom built to specification.

Further information on the All-Purpose extinguisher or available cabinet styles will be supplied free on request from The Fyr-Fyter Co., 221 Crane St., Dayton 1, Ohio.

▶ A new tin-lined goose-neck distilled water faucet, recently announced by Barnstead Still & Sterilizer Co., is designed for mounting on laboratory benches to maintain purity of distilled or demineralized water to point of use.

The faucet is constructed of brass, lined with pure block tin to prevent metallic contamination. It is finished in polished nickel to blend with other laboratory accessories. Manufacturer states that the goose-neck faucet is ideally suited for distilled water distribution systems.

Further information may be obtained by writing to Barnstead Still & Sterilizer Co., 168 Lanesville Terrace, Boston 31, Massachusetts.

▶ A new integrated proportional counting system called the Logic 802 has been announced by Nuclear-Chicago Corp., of Des Plaines, Illinois. The Logic 802 incorporates four chassis in a single unit to provide linear amplification, scaling, timing, and high voltage for G-M counting or for proportional and scintillation counting with integral pulse-height analysis. A cooling base with forced air flow and a separate preamplifier are also supplied.

The Model 802 has provision for connecting a digital recorder, a linear ratemeter, a logarithmic ratemeter, and a graphic recorder. The individual com-

(*Continued on page A409*)

*Universally Accepted . . . Universally Used*

High Quality • Versatile • Sensitive

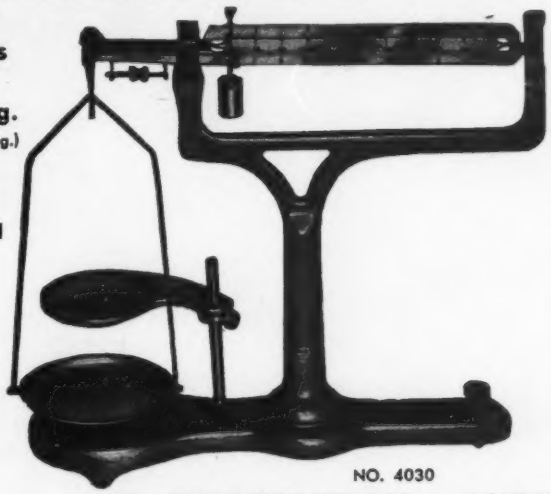
**WELCH TRIPLE-BEAM BALANCE**

**All Exposed Parts of *Stainless Steel***

**SENSITIVITY**
**0.01 g. or less**

**CAPACITY 111 g.**
(With extra weight 201 g.)

- Fast Weighing
- Accuracy-tested
- Corrosion-Resistant
- Economical
- Wide-Range
- Convenient
- Low Cost



NO. 4030

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| 4030. | TRIPLE-BEAM BALANCE, High Form. | Each $87.50 |
| 4031. | AUXILIARY WEIGHT. | Each $1.50 |
| 4030C. | PLASTIC COVER for No. 4030. | Each $1.60 |

**THE WELCH SCIENTIFIC COMPANY**

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*Manufacturers of Scientific Instruments and Laboratory Apparatus*

**instant, positive,**

**Gas Detector**

**with BROTHERS test proven Detection Kit**

- Sensitive well below the mac* range
- Consistant results
- Easy to use
- Wide choice of tubes

Don't take chances with poisonous and deadly vapors and gases. This easy-to-use, precision instrument will tell you when dangerous environment exists . . . down to a few PPM. Send for complete literature.

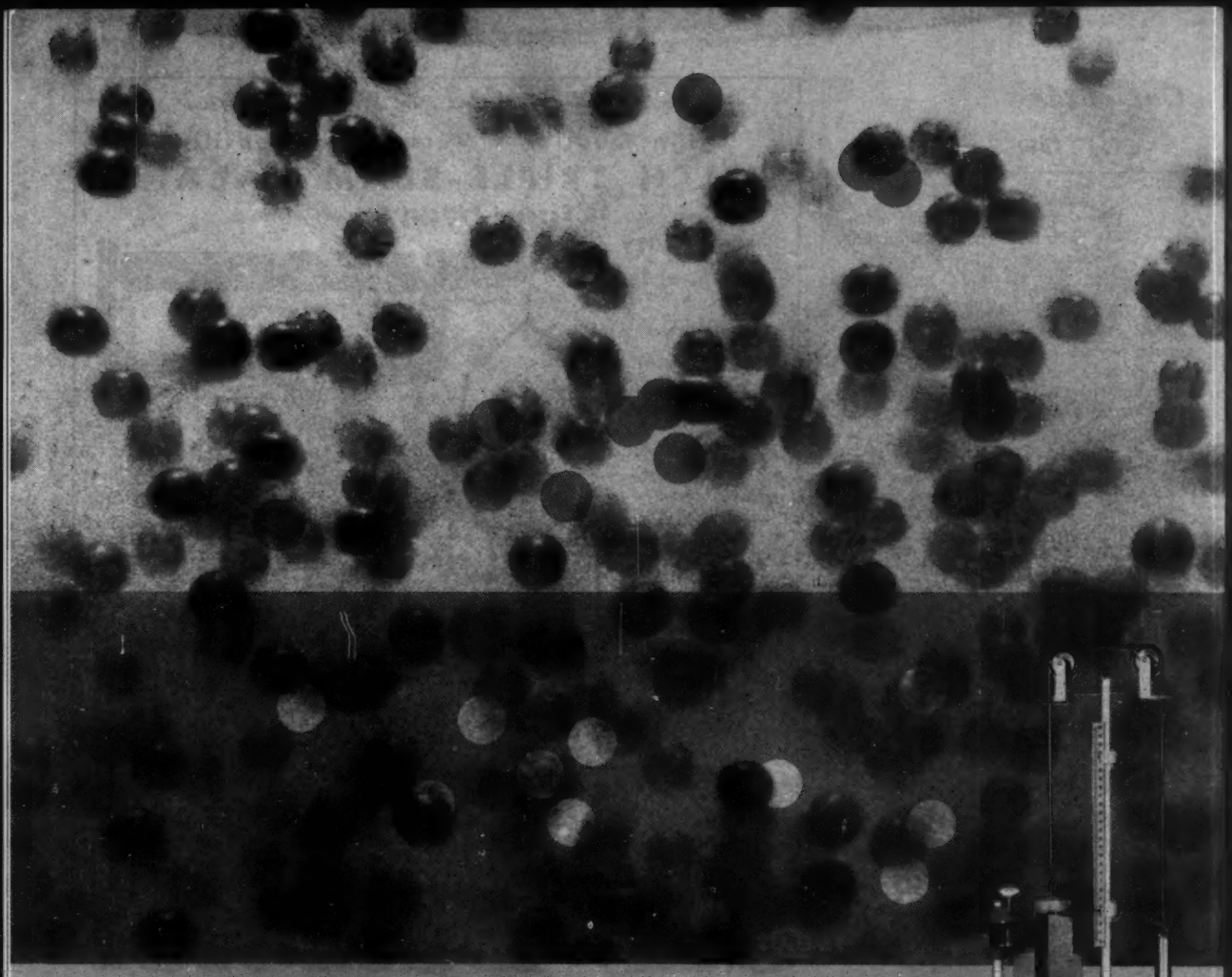
* MAXIMUM ALLOWABLE CONCENTRATIONS for exposure during an eight hour day adopted at the 22nd annual meeting of the American Conference of Governmental Industrial Hygienists.

**$ 85.00**
COMPLETE with pump, remote sampler and one hundred tubes in sturdy leather case.

BROTHERS CHEMICAL

**BROTHERS CHEMICAL CO.**

ORANGE, NEW JERSEY

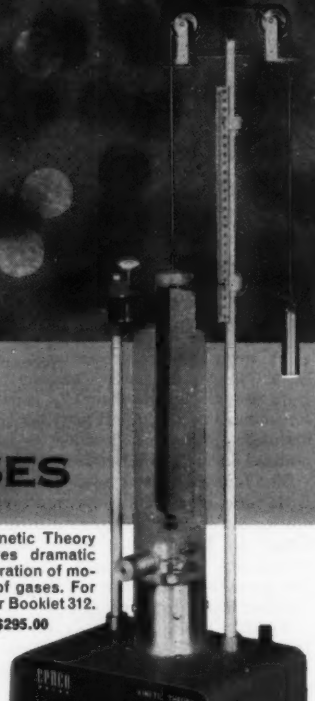


# NOW YOU CAN SEE SIMULATED MOLECULAR ACTION OF GASES

Cenco has developed a new device designed to demonstrate the most fundamental principles of gas mechanics. Quantitative results as well as visualization are obtained. The Cenco Kinetic Theory Apparatus is an excellent instructional device used for studies and experiments in connection with Boyle's Law, Van der Waals' Corrections and Avogadro's Law.

As in a real gas, the test gas in the Kinetic Theory Apparatus is composed of molecules; however, these "molecules" are plastic balls of $\frac{1}{8}$" diameter. The concentration of "molecules" may be varied by the quantity used. Movement is obtained by a motor-driven impeller disk. The Cenco Kinetic Theory Apparatus is adapted from a model developed by Prof. Harry M. Meiners of Rensselaer Polytechnic Institute.

This is another example of new ideas from Cenco for teaching fundamentals in physics.



New Cenco Kinetic Theory Apparatus gives dramatic visual demonstration of molecular action of gases. For details, write for Booklet 312.

No. 77722 **$295.00**

cenco

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*A Division of Cenco Instruments Corporation*

**1718-E Irving Park Road • Chicago 13, Illinois**

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*Somerville, Mass. Toronto Los Angeles*
*Birmingham, Ala. Ottawa Vancouver Houston*
*Cenco S.A., Breda, The Netherlands Tulsa*

## *Out of the* EDITOR'S BASKET

ponents of the 802 system may also be purchased separately.

Detailed information and specifications are available on request.

▶ Two new portable models have been added to the line of laboratory safety shields manufactured by Instruments for Research and Industry, 108 Franklin Ave., Cheltenham, Pennsylvania, under the trademark Lab - Guard. The manufacturer states that the portable shields are both of a compact weighted-base type, but differ in size and shape.

These new Lab-Guard shields employ quarter-inch-thick transparent Plexiglas acrylic plastic in the viewing portion of the guard and are said to combine dependable protection with greatly improved convenience of use on the laboratory bench. The curved shape provides shielding at the sides as well as directly in front of the guard.

The new Lab-Guard models were developed to meet the need for a device which will provide dependable protection, permit full visibility of apparatus, be easy to reach around, and yet be easily moved from place to place in the laboratory.

▶ A new infrared bath, accurate to ±0.005°C by means of a thermistor sensor and transistorized relay control circuit is available from Labline, Inc., 3070–82 W. Grand Ave., Chicago, Illinois.

The "Hi-Accuracy" Bath, as it is called, has a temperature range from 5 to 60°C and provides 98% free work area in the bath—using 12-in. diameter Pyrex jars, either 12 or 18 in. high. The bath may be used either as a source of tempered fluid or as a medium in which to work directly. The new design eliminates the need for immersion heaters, internal stirrers, vibrating pens or magnets.

For full information, write for *Bulletin No. 6.*

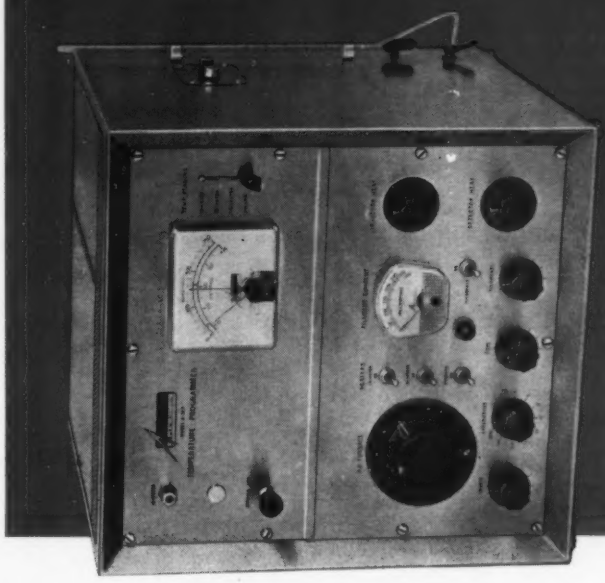
▶ Cenco's No. 79549 Low Voltage Power Supply, a compact and convenient new low voltage power supply unit for operating small motors, electromagnets, electroplating and electroanalysis experiments, charging batteries and lighting lamp filaments is now available. The circuit is built around a transformer, a dry disc rectifier and a combination wirewound rheostat and switch, offering quiet, shock-resistant performance. The unit also features extra large, universal output terminals which accept all common electrical connectors.

For additional information about the Cenco No. 79549 Low Voltage Power Supply write to Central Scientific Co., a division of Cenco Instruments Corp., 1700 Irving Park Rd., Chicago 13, Illinois.

▶ A new microfilm reader, the Dagmar Super, for the first time makes possible the table top reading and wall projection of all types of microfilm on one unit. The types of micro-records which can be read on the Dagmar Super include 35 milli-

(*Continued on page A410*)


WILKENS INSTRUMENT & RESEARCH INC. / P.O. Box 313, Walnut Creek, Calif. Phone ATlantic 4-7166



AEROGRAPH A-90-P

A NEW STANDARD IS SET FOR GAS CHROMATOGRAPHY INSTRUMENTS

The Aerograph A-90-P, a manual temperature programmed gas chromatograph, is a new version of the well-tested Model A-90-C. It embodies features which make it an outstanding tool for modern day Research and Control work.

Of special interest is the separately heated ovens for the column and detector cell. With this arrangement the column oven may be manually temperature programmed with greatest ease. Isothermal operation is also excellent. Temperatures of the column oven, detector cell, and injector are indicated on the accurate, compensated pyrometer.

Sample collection is very effective. The stainless steel collector tube is controlled by the detector cell temperature preventing sample condensation during passage from the cell to the appropriate collection device.

The detector cell is stainless steel, four-filament with the reference side at atmospheric pressure. It is located conveniently for cleaning or replacing filaments. A built-in D.C., solid state power supply eliminates need for any battery. The efficient Aerograph Flame Detector Kit adapts perfectly to the A-90-P.

- COLUMN OVEN—Variable 350°C with fan for air circulation and cooling.
- INJECTOR—Stainless steel, with adjustable temperature to 400°C.
- DETECTOR OVEN—Cast aluminum with large thermal mass, separately heated to 400°C.
- POWER SUPPLY—Built-in, completely solid state, DC 12 volt, and very stable. No batteries are needed.
- SENSITIVITY CONTROL—Nine step precision attenuation reduces signal by half each step 1 to 500. Accuracy 1%.
- COLUMN INSTALLATION—Easy and rapid with Swagelok fittings. Length to 50 feet.
- MANUAL OVEN CONTROL—Rapid heating and cooling rate.
- AEROGRAPH FLAME DETECTOR KIT—Easily mounted for ultra sensitivity.

The Aerograph A-90-P is recommended as an all-purpose gas chromatograph with a wide range of flexibility. Its small size makes it especially desirable for the crowded bench. Your order by phone or letter will receive prompt attention.

WRITE FOR YOUR FREE SUBSCRIPTION TO AEROGRAPH RESEARCH NOTES FOR SPECIAL DETAILS ON GAS CHROMATOGRAPHY APPLICATIONS.

## *Out of the* EDITOR'S BASKET

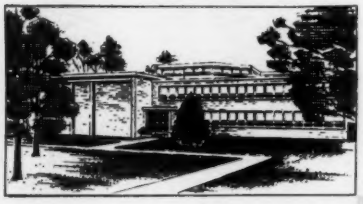
meter roll-film, 16 millimeter roll-film, 3 × 5 in. microsheet (known in Europe as microfiche), jacket mounts, and aperture cards including Remington Rand's Microseal and Minnesota Mining & Manufacturing's Filmsort systems.

The Dagmar Super is easily portable being only 9 in. x 9 in. x 10 in. closed and weighing only 16 pounds. (Most mode's are $139.50) Dagmar Super is manufactured in Holland and distributed in America by Audio-Visual Research of 523 So. Plymouth Court, Chicago 5, Illinois, and Box 71, Waseca, Minnesota. Descriptive material is available on request.

▶ A new Recording Titrator, the Model D, for all potentiometric and *p*H titrations has been developed by E. H. Sargent & Co. This is an all purpose automatic and potentiometric recording titrator with dual, motor driven titrating assemblies, multiple direct reading *p*H and millivolt ranges and an automatic rate sensing and adjusting system to prevent curve distortion in slow reaction systems.

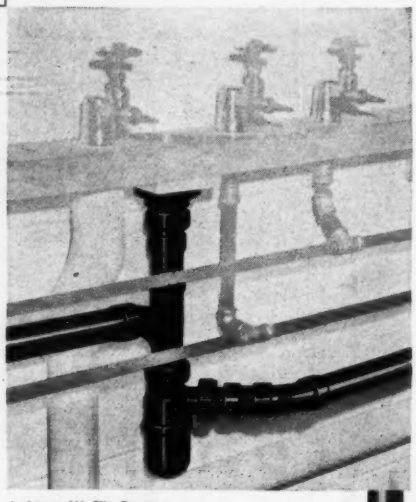
The Model D can be used for all types of potentiometric titration, with either glass or metal electrode systems, in which end points are determined either from a recorded curve or by automatic interruptions of titrations at a predetermined *p*H or voltage value.

For complete information on this Recording Titrator, please write to Dept. RT, E. H. Sargent & Co., 4647 W. Foster Ave., Chicago 30, Illinois.

*How do you drain 25,000 sq. ft. of chemical lab space?*

**Hercules Powder chose Vulcathene® drainlines for their new Wilmington Research Center**



Architect: W. Ellis Preston
Contractor: Ernest DiSabatino & Sons, Inc.
General Plumbing Contractor: William D. Shellady, Inc.

This much lab space produces torrents of corrosive wastes—and Hercules Powder Company installed Vulcathene pipe*, cup sinks, traps and fittings to handle the job.

Why? Because Vulcathene provides acid-proof, shatter-proof protection in a completely integrated, maintenance-free drainage system of virgin polyethylene. It's scale-proof, clog-proof, lightweight, noncorrosive—perfect for the job.

Best of all, Hercules was able to install Vulcathene at about a quarter of the cost of other materials.

Think it over. It'll probably pay you well to think about Vulcathene for your drainage needs. There's a new catalog to tell you all about this completely integrated system—in sizes from ½" to 6". Also a list of hundreds of users. Just write Dept. 346.

*Made with Hi-Fax—Hercules Powder Company's Registered Trademark for high-density polyethylene.

SEE OUR CATALOG IN SWEET'S

American Vulcathene
P.O. BOX 365 ROCHESTER 2, NEW YORK
DIVISION OF THE NALGE CO. INC.


▶ A new decade scaler, especially designed for low activity counting and for training use, is announced by ATOMasters-Buntaine Corp., 111 W. Jewel Ave., St. Louis 22, Missouri. Designated Model 100, the scaler features five decades, printed circuit, 2500 v supply with time delay to protect the detector, and built-in elapsed timer. Controls are push button for greatest convenience. Vacuum tubes are used throughout. The chassis is provided with simple check points and complete service information.

## New Literature

● A new and enlarged radiochemical catalogue said to contain the industry's most complete and comprehensive selection of carbon-14 and tritium labeled compounds for research purposes is now available from New England Nuclear Corp., 575 Albany St., Boston 18, Massachusetts. Listing of labeled compounds containing short-lived isotopes, such as Iodine 131, Phosphorus 32, and Sulfur 35, and compounds labeled with stable isotopes such as Deuterium are included.

● Buck Engineering Co., Inc., Freehold, New Jersey, offers a new catalogue *Lab-Volt, Power Stations, for Educational Laboratories and Shops.*

● A new, 12-page brochure technical *Bulletin No. 1* describing the properties and characteristics of Ameripol Polyethylene—a new ethylene plastic polymer that combines durability with processability—has been published by Goodrich-Gulf Chemicals, Inc., 1717 E. Ninth St., Cleveland, 14, Ohio.

● A new 12-page, three-color bulletin *No. 1960* entitled *Blue M Power-O-Matic 60 Mechanical Convection Ovens with Blue M Saturable Power Reactor Control* is available from Blue M Electric Co., 138th and Chatham St., Blue Island, Illinois.

● Olin-Mathieson Chemical Corp., 460 Park Ave., New York 22, N. Y., offers *Toward Discovery, Olin Research* a most interesting new brochure. The variety of research expenditures in chemicals, energy, metals, packaging, pharmaceuticals and sporting arms, and ammunition are discussed.

● Hygrodynamics, Inc., is a new corporation created to expand and maintain the activities formerly performed by the Hygrometer Division of the American Instrument Co., Inc., *Catalogue 661, Precision Measurement and Control of Relative Humidity* is now available from their office at 949 Selim Rd., Silver Spring, Maryland.

● *The Costly Time Lag,* Publication *No. 813* containing facts about the unnecessary loss of life, health, and money that results from failure to use new research findings was recently released by the Public Health Service, Washington 25, D. C. Single copies are available on request.

● A comprehensive 40 page reference handbook on the properties and uses of aluminum sulfate has just been published

(*Continued on page A412*)

# NEW TORSION DIAL BALANCES with WEIGHT LOADERS

Torsion's new line of weight-loading dial balances retains all the proved advantages of the unique Torsion principle which eliminates knife edges and guarantees long-lasting accuracy.

Since Torsion introduced the "fine weighing" dial over a year ago, users have reported substantial savings in weighing time. Now Torsion has added a "weight-loading" dial which enables the user to "dial in" additional weights as described in the specifications for each new balance.

Both dials can be used without arresting the balance.

By using two dials, one for weight loading and one for fine weighing, Torsion has cut weighing time even more.

With Torsion's new two-dial feature, the time-consuming handling of small, loose weights has been eliminated. In addition to faster weighing, Torsion's new dial balances with weight loaders minimize the possibility of weights becoming inaccurate from rough handling.

Ask your laboratory supply salesman for a demonstration or write for complete specifications.

*The* **Torsion Balance** *Company*

Main Office and Factory: Clifton, New Jersey
Sales Offices: Chicago, Ill., San Mateo, Calif.

**A TORSION MODEL DWL-3**
**Capacity:** 200 grams
**Weight-loading Dial:** up to 9 grams by 1 gram increments
**Fine Weighing Dial:** 1 gram by .02 gram graduations
(Readability: .005 g)

**B TORSION DWL-5**
**Capacity:** 500 grams
**Weight-loading Dial:** up to 90 grams by 10 gram increments
**Fine Weighing Dial:** 10 grams by .1 gram graduations
(Readability: .02 g)

**C TORSION DWL-2**
**Capacity:** 120 grams
**Weight-loading Dial:** up to 9 grams by 1 gram increments
**Fine Weighing Dial:** 1 gram by .01 gram graduations
(Readability: .002 g)

**TORSION DWL2-1**
Specifications are same as the DWL-2 except that this model has scoop for seeds or other bulky material.

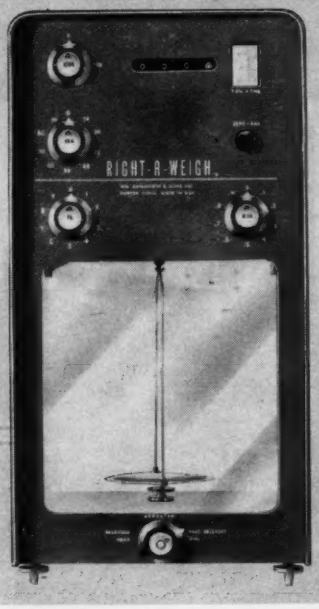
# AINSWORTH

## Premium Quality at Competitive Price

Made in U.S.A.

**RIGHT • A • WEIGH**

*Substitution Weighing Balance*




**FAST**
**ACCURATE**
**EASY TO USE**

**CONTROLS**

All controls on front of case, clearly designated. Independent pan brake stabilizes the pan before beam is released. Simple mechanical zero adjustment, large range, no distortion. Easy-working doors with comfortable finger-grips.

**READOUT**

Eye-level, in-line, unobstructed readout. Wide-spaced lines on projected scale. Projection scale in recessed shadow box. Light filter in optical path cuts out glare.

***FAST*** *...weighing procedure is simply to load pan, dial weights, read results.*

***ACCURATE*** *...substitution weighing eliminates arm-length errors, gives constant sensitivity and accurate values.*

***EASY TO USE*** *...anyone can weigh quickly and accurately with the Right-A-Weigh ...frees skilled people for other work.*

Capacity: 200 g. Sensitivity: 1/10 mg. Readability: 1/20 division on projected scale using vernier. Reproducibility: ±0.03 mg.

Special Models: SCX, explosion proof; SCD, diamond balance calibrated in carats; SC 300, 300 gr. cap.

AINSWORTH

**WRITE FOR BULLETIN 659.**

*Symbol of Quality & Progress Since 1880.*

WM. AINSWORTH & SONS, INC.
2151 LAWRENCE ST. · TELEPHONE ALpine 5-1723 · DENVER 5, COLORADO


## *Out of the* EDITOR'S BASKET

by Stauffer Chemical Co., 380 Madison Ave., New York 17, N. Y.

● Requests for *Catalogue 109,* a comprehensive compilation of 38,000 items alphabetically arranged with a permanent catalogue number and up-to-date illustrations are now being honored by E. H. Sargent and Co., 4647 W. Foster Ave., Chicago 30, Illinois.

● Metal Hydrides Inc., *Technical Bulletin 509,* just published, describes the treatment of glycols and polyglycols with sodium borohydride to remove trace carbonyl impurities. Treating techniques are summarized and the economics of the reduction are discussed in detail. Write Metal Hydrides, Inc., 12–24 Congress St., Beverly, Massachusetts.

● *Platinum Metals Review,* Volume 5, Number 2, April, 1961, may be obtained from J. Bishop and Co., Platinum Works, Malvern, Pennsylvania.

● *X-Ray Protection Up to Three Million Volts,* National Bureau of Standards Handbook 76 (supersedes H60) prepared by Subcommittee 3 of the National Committee on Radiation Protection and Measurement. Issued February, 1961, 52 pages, 25 cents. (Order from Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C).

● The following are available from the OTS, U. S. Department of Commerce, Washington 25, D. C.:

SB-447 *Fuel Cells and Related Research.* This bibliography lists 80 reports of the Army, Navy, Air Force, Atomic Energy Commission, and other Government agencies, as well as foreign technical literature, pertaining to fuel cells and related research. Material listed includes such subjects as batteries, electrical power sources, electrochemistry, advanced propulsion systems, and state-of-the-art fuel cell studies —10 cents.

TID-6374 *Radioisotope Experiments for the Chemistry Curriculum.* Nuclear-Chicago Corp. for the U. S. Atomic Energy Commission. August, 1960. 162 pages, $2.

AEC-tr-3976 *The Chain Mechanism of the Decomposition of Halogenated Paraffins,* 114 pages. $1.25.

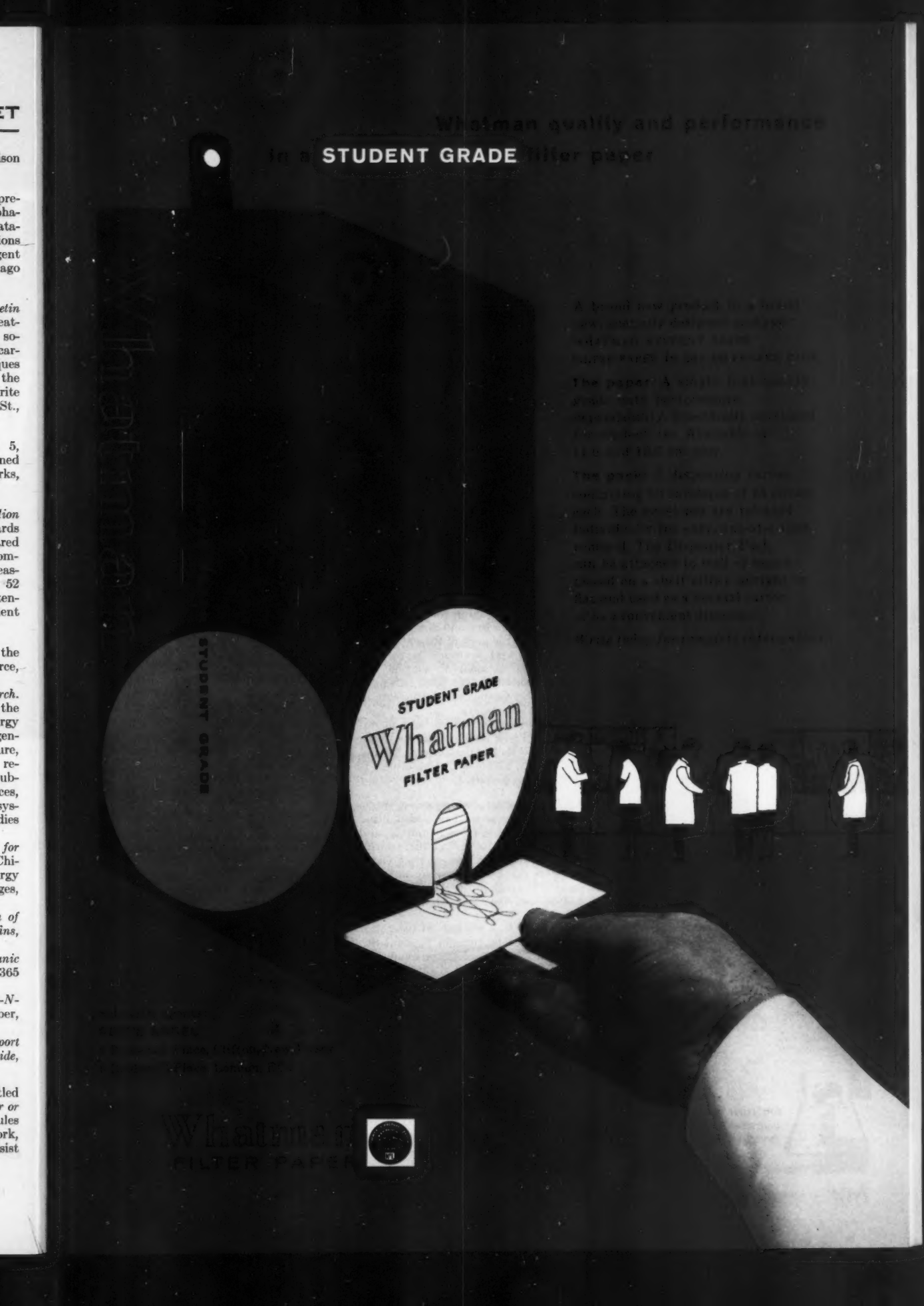
AEC-tr-4051 *Journal of Inorganic Chemistry:* Volume 2, No. 1: 1957, 365 pages, $3.75.

DP-513 *Nitric Acid Species in Tri-N-Butyl Phosphate Solutions,* September, 1960, 29 pages, 75 cents.

GA-1038 *Thermodynamic and Transport Properties of Gaseous Carbon Dioxide,* August, 1959, 157 pages, $2.75.

● A very informative little booklet entitled *Guide to the Correct Selection of a Timer or Chronograph* is available free from Jules Racine & Co., 20 W. 47th St., New York, N. Y. This booklet is designed to assist

*(Continued on page A414)*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## *Out of the* EDITOR'S BASKET

in the selection of the proper time piece for any specific need. A "glossary of terms" common to the watch industry is also provided to help evaluate certain features in relation to individual needs."

● A new catalogue, listing an expanded line of MC&B laboratory chemicals has just been published by the Matheson Coleman & Bell Division of The Matheson Co., Inc.

The catalogue contains over 5000 laboratory listings, including organics, inorganic reagents and elements, and a comprehensive line of stains and indicators.

Several hundred new items are listed, including a new line of Chromatoquality chemicals for gas-liquid chromatography. The catalogue is being offered by MC&B distributors, or may be obtained by mail from Matheson Coleman & Bell, P.O. Box 85C. East Rutherford, New Jersey.

### New Chemicals

◇ Standard solutions for use in titration procedures are prepared directly from the 38 volumetric concentrates in the newly available Chemtam line. These include all commonly used materials as well as EDTA as a sodium salt.

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The Chemtam ampoules are manufactured by P. H. Tamm Co. of Altuna, Sweden. Bio-Rad Laboratories, 32nd and Griffin Ave., Richmond, California, is their U. S. representative.

◇ Applied Science Laboratories, State College, Pennsylvania, has added ethyl oleate, ethyl sterate, ethyl palmitate, and ethyl caproate to its line of high purity (99 + %) fatty acid derivatives. Other ethyl esters can be synthesized on order. Because of the high purity, these materials should be useful as gas chromatography standards.

◇ Pilot Chemicals, Inc., 36 Pleasant St., Watertown 72, Massachusetts, announces the manufacture of a new peptide-former, *N*-ethyl-5-phenylisoxazolium-3′-sulfonate (Woodward's Reagent K.) This material was first synthesized and its application for forming peptides was developed by R. B. Woodward, R. A. Olofson, and H. Mayer at Harvard University.

◇ The J. T. Baker Chemical Co., Phillipsburg, New Jersey, announces an "industry-first" packaging advance with the introduction of the new Adjusta-Flow 1 lb container for "Baker Analyzed" Reagent Hydrofluoric Acid.

(*Continued on page A416*)

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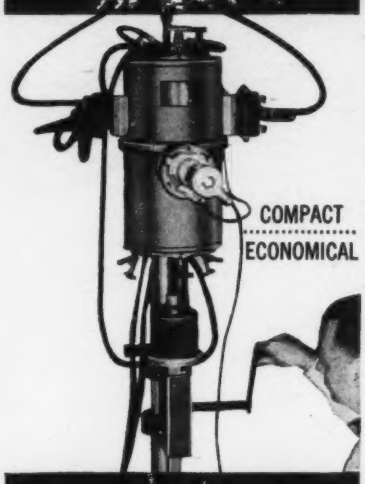

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## *Out of the* EDITOR'S BASKET

◇ Chemical Service Laboratories, P.O. Box 281, Largo, Florida, announces the introduction of their "Standardettes" . . . chemical standards which permit laboratory technicians to accurately standardize titrating solutions to four-figure accuracy in a matter of minutes.

### Miscellany

★ Education is expensive but the failure to use knowledge already accumulated and evaluated is also very expensive. The following figures from *The Costly Time Lag* published by the U. S. Department of Health, Education and Welfare are astounding:—40,000 cancer deaths which could have been prevented occur every year—40 million children are growing up without the protection from tooth decay afforded by fluoridated water—20,000 persons die each year from preventable attacks of rheumatic fever and rheumatic heart disease—60,000 new cases of tuberculosis occur every year although ways of preventing its spread are well known—17 million persons have some type of chronic disability and a high proportion fail to receive care that could reduce handicapping effects.

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★ The National Bureau of Standards has prepared trimethylborane in a more highly-purified form than had previously been available. This compound was needed in such pure form for use as a neutron capturing gas in proportional counters and as a subject of thermodynamic investigations conducted by the Bureau. The gas was liberated from the solid ammonia adduct by reaction with specially prepared hydrogen chloride. Cryoscopic analysis indicated a purity of 99.9 mole per cent.

★ According to *"Glycerine Facts"* even ravioli now contains a plasticizer and it is, as expected, glycerine. Patent No. 2,950,978 covers the use of from 3-159, glycerine, based on the dry weight of flour used prevents the cracking of individual ravioli after drying.

★ A center for the collection and evaluation of data on atomic transition probabilities and cross sections has been established at the National Bureau of Standards. The center will compile atomic data in areas where experimental or theoretical investigations are being conducted at NBS. This compilation has been started as part of a research program, sponsored by the Office of Naval Research and the Advanced Research Projects Agency, which seeks to supply the data needed for current and future research in plasma physics and astrophysics.

In order that the data center may be as effective and up to date as possible, authors are urged to send preprints and reprints of pertinent publications to The Atomic Physics Data Center, Far West Building, National Bureau of Standards, Washington 25, D. C.

★ The Atomic Energy Commission has available for free-loan or purchase a new, 57 minute color motion picture, "Industrial Applications of Radioisotopes." The 16 mm. semitechnical film is a survey of the current wide spread uses of radioisotopes in American industry. The film is available from the Commission's ten domestic film libraries.

★ The Fifth Annual Symposium on Advances in Tracer Methodology will be held at the Shoreham Hotel in Washington, D. C., on Friday, October 20, 1961. These symposiums are sponsored by New England Nuclear Corp. to provide an annual review of and discussions on new developments in the use of radioactive isotopes as "tracers" for research purposes. For further information contact: Paul A. McNulty, New England Nuclear Corp., 575 Albany St., Boston 18, Massachusetts.

★ "Probability: The Odds Are High That It Affects You" is the title of an article by Warren Weaver in the April, 1961, issue of *Think* the International Business Machines Corp. publication. He says, "The mathematics to which our youngsters are exposed to in high schools is, with rare exception, based on the classical yes-or-no, right-or-wrong type of logic. It normally doesn't include one word about probability as a mode of reasoning or as a basis for comparing several alternative conclusions." *Do we college and university chemistry professors do any better?*

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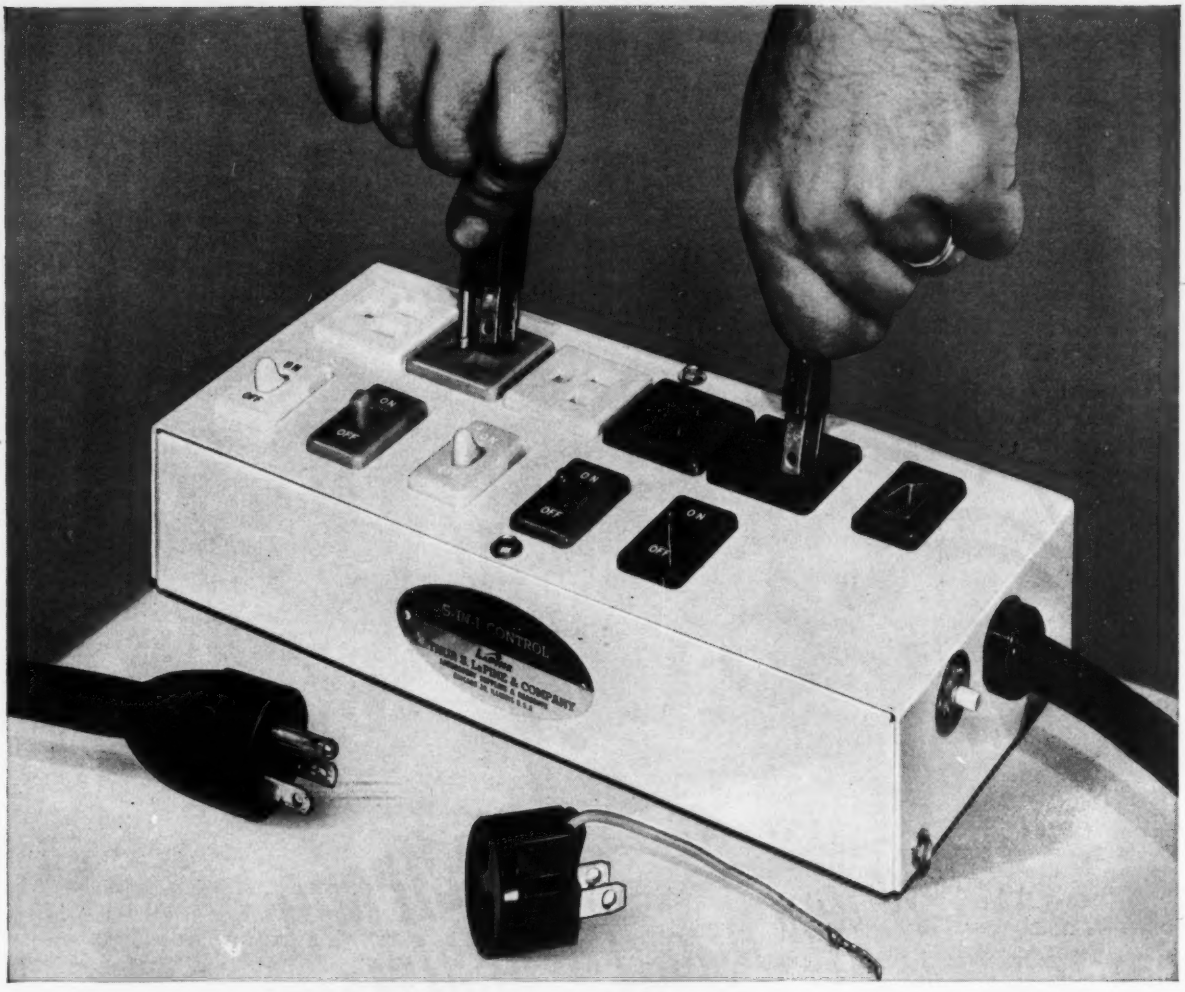


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# PREPARATION OF METALLIC LITHIUM

A Chem Ed TESTED DEMONSTRATION

*Submitted by:* Saul L. Geffner, Forest Hills High School, New York
*Checked by:* Julian R. Brandou, Michigan State University

## PREPARATION

Prepare a melt of (50–75 g) LiCl in an iron crucible. Use a $^1/_4$-in. graphite rod anode and a heavy iron ($^1/_{16}$-in. piano wire) cathode, the end of which has been bent to form a loop 1 cm in diameter. Provide heat source and 6 v dc.

## DEMONSTRATION

Carefully heat the crucible until the LiCl melts and then reduce the flame. Insert the electrodes so that the loop is completely immersed in the molten salt. Electrolyze for several minutes and carefully withdraw the loop filled with metallic lithium.

## REMARKS

Care should be taken to avoid overheating the melt, as this increases the difficulty of removing the filled loop.



# SILVER PLATING FROM AN IODIDE COMPLEX

A Chem Ed TESTED DEMONSTRATION

*Submitted by:* Saul L. Geffner, Forest Hills High School, New York
*Checked by:* Julian R. Brandou, Michigan State University

## PREPARATION

Prepare the complex solution by the addition of saturated KI solution to a 0.5 *M* (approximate) $AgNO_3$ solution until all AgI *just* dissolves. Provide a small porous cup, a $^1/_4$-in. graphite rod anode, a source of controlled emf (0–3 v is sufficient for small objects) and a clean item to be plated.

## DEMONSTRATION

With the anode in place within the porous cup and the object to be plated as the cathode, electrolyze the solution for several minutes at a current density of approximately 0.1 amp/in.$^2$ of surface. Plating is clearly visible as it forms in the clear solution and may be carefully buffed to a metallic luster.

## REMARKS

The porous cup serves to prevent contamination of the plating solution by free iodine. This cell operates nearly as well as the toxic cyanide complex system and with much less danger. As in all plating procedures, current density and surface conditions greatly affect the quality of the plating.

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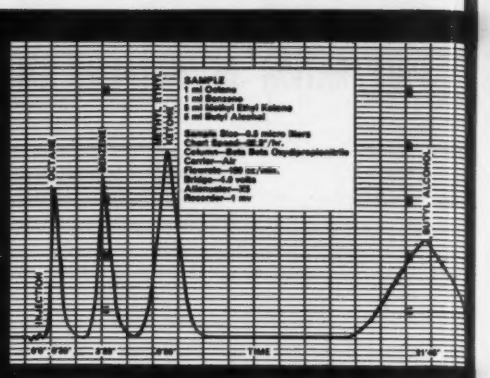


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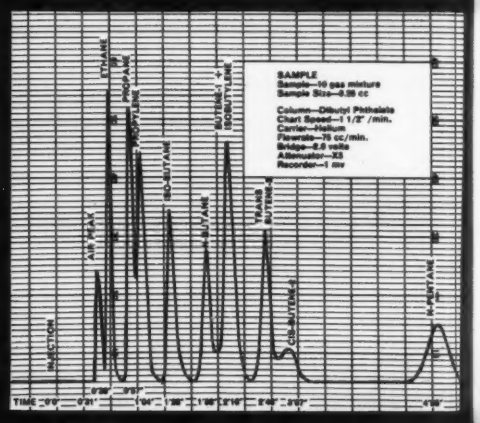


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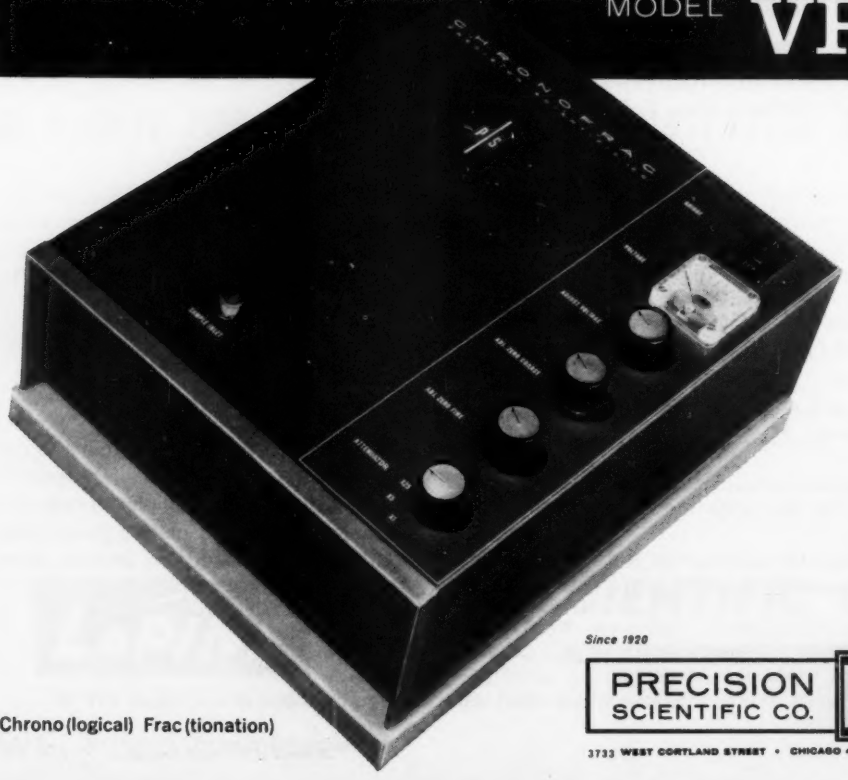


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# CHEMICAL PROJECTS

## *Research Ideas for Young Chemists*

Compiled by **JAY A. YOUNG,** Kings College, Wilkes-Barre, Penna.
**JOHN K. TAYLOR,** National Bureau of Standards, Washington, D. C.

## Simple Method for the Preparation of Tertiary Amines

*See* BUTLER, G. B., AND BENJAMIN, B. M., *J. Chem. Educ.*, **28**, 191 (1951).

Tertiary amines can be prepared without the use of a high pressure autoclave and anhydrous ammonia, contrary to statements in some organic chemistry texts which imply that reactions between alkyl halides and aqueous ammonia are impractical at ordinary pressures. Three tertiary amines have been prepared; an explicit procedure for the preparation of triallyl amine from allyl bromide and aqueous ammonia is given as a typical example. Many other tertiary amines can, no doubt, be prepared by a similar method. For investigational purposes, it is recommended that the quantities cited by Butler and Benjamin be reduced to about $^1/_{10}$ the amounts indicated.

**Questions:**

Prepare one of the tertiary amines described by Butler and Benjamin; isolate and identify as many of the side products as possible.

Prepare any other tertiary amine by the procedure indicated, adjusting the conditions so as to obtain a maximum yield.

What derivatives can be formed from the tertiary amine you have prepared?

Can the amount of side products formed be reduced by suitable modifications of the procedure described by Butler and Benjamin?

Can tertiary amines be prepared by any other procedure which does not require the use of an autoclave?

Is it necessary that the organic reactant be a halide? Would some other compound, such as a cyanide, an alcohol, or perhaps a mercaptan, or other hydrocarbon derivative, also be suitable? If not suitable, suggest reasons why and test these reasons by further laboratory investigations.

## Friedel-Crafts Reaction in Elementary Organic Laboratories

*See* WRIGHT, O. L., FUHLHAGE, D., AND SHERIDAN, E., *J. Chem. Educ.*, **29**, 620–21 (1952).

Many different Friedel-Crafts reactions can be run in an ordinary test tube and the product separated by fractional distillation from the reactant mixture. Though there is some fire hazard because carbon disulfide is used as a solvent, the technique described minimizes this problem sufficiently. Students who perform this work should also be cautioned to avoid breathing benzene (and other aromatic) vapors since these vapors are poisonous and their effect is partly cumulative. Wright, *et al.*, list twenty different reactions, of which eighteen were for ketones.

**Questions:**

Carry out one of the reactions described and identify the major products, after isolation, by preparing a suitable derivative whose characteristics can be measured and compared with its properties as described in the literature.

Can the major product of any selected reaction be separated by a procedure not involving fractional distillation?

Select three or more homologous hydrocarbons and, using the same acylating agent for each, determine the variation necessary in the conditions to produce a maximum yield of product in each case.

Select three or more homologous acylating agents and, using the same hydrocarbon, determine the variation necessary in the conditions to produce a maximum yield of product in each case.

Select a hydrocarbon and an acylating agent not listed in the article and prepare a ketone by the procedure described by Wright, *et al.* Identify and characterize this product.

## Preparation of 2-naphthaldehyde

*See* DOUKAS, H. M., *J. Chem. Educ.*, **31**, 12 (1954).

By bromination of 2-methylnaphthalene with *n*-bromosuccinimide, followed by condensation of the crude bromide with hexamethylenetetramine, 2-naphthaldehyde can be prepared. This procedure is an improvement over other methods reported in the literature. The product, as well as other 2-substituted naphthalene compounds, has plant growth regulating properties and can be used for studies of the factors affecting plant growth.

**Questions:**

Prepare 2-naphthaldehyde by one or more of the other procedures mentioned in the references to Doukas' article and compare the advantages and disadvantages of each such method. (If not available locally, copies of the articles describing these other procedures can be obtained from libraries holding the appropriate journals upon application in the usual way or by writing to an author, requesting a reprint.) Verify the composition of the intermediate product, a hexammonium bromide compound, by analysis for halogen content. Verify the composition of the final product by similar means.

Prepare aldehydes of other polynuclear hydrocarbons such as 2-methylanthracene, 2-methylphenanthracene, or 9-methylanthracene and determine if they are growth regulators.

From a study of the earlier procedures and a comparison with Doukas' method, devise a different (and improved) procedure for the preparation of 2-methylnaphthaldehyde.

*(This investigation is particularly suitable for the student who wishes to combine an interest in German with his work in chemistry. Also, as indicated, it can be used as a combined chemistry-biology project.)*

## Detecting Nitrite and Sulfamate Ions in Qualitative Analysis

*See* BRASTED, R. C., *J. Chem. Educ.*, **28**, 592–3 (1951).

Sulfamic acid reacts with nitrite ion to form hydrogen sulfate ion, nitrogen, and water. Hence, the evolution of a gas when either reagent is added to a solution suspected to contain the other probably indicates the presence of the suspected substance. Other possible gaseous products (from other components), such as hydrogen sulfide, carbon dioxide, etc., can be identified readily; in addition, the hydrogen sulfate ion, which is also formed when sulfamate or nitrite is present and the corresponding alternate reagent added, can be identified by a second confirmatory test.

Possible interferences due to other ions and methods for elimination of such effects are discussed.

**Questions:**

Can the interfering effects of any of the ions mentioned by Brasted be eliminated by procedures other than those described in the article?

Can you find any ions, in addition to those mentioned, which will interfere with this test for nitrite or sulfamate ion; can you devise a suitable procedure to eliminate this interference?

There are many pairs of substances, such as silver ion and chloride ion; either can be used to test for the presence of the other ion. As in the case described here for sulfamate and nitrite ion, however, interferences from other substances often complicate or preclude the use of these simple tests for the presence of either member of the pair. Select any suitable pair of substances and devise procedures to eliminate the effects of any other substances which would otherwise interfere.

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## The Use of Starch-Iodate Paper in Qualitative Analysis

*See* LUNDIN, J. A., *J. Chem. Educ.*, **28**, 122 (1951).

Starch-iodate paper turns blue when exposed to sulfur dioxide. It is prepared by moistening a piece of filter paper with a drop of each of the following solutions: starch, potassium iodate, and dilute nitric acid. This test paper can be used to distinguish between carbonate and sulfite; other distinguishing tests are less simple.

**Questions:**

Are there any other gases, in addition to sulfur dioxide, which will cause the paper to turn blue? If so, how can these interferences be effectively eliminated when this test paper is used in qualitative analysis?

Lundin states that as little as 0.3 mg of sulfite ion can be detected by this method. Does the concentration of the 0.3 mg of sulfite ion make any difference?

What is the sensitivity of this test paper and is this value altered by varying the concentration of the solutions, or the amounts, used in the preparation of the test paper? Account for any such effects, if found.

Lundin states that starch-iodate test paper can also be used to identify several ions, directly, in solution. Can you prepare still other test papers which will distinguish between these several ions, once the starch-iodate test paper indicates that one or more of them is present in solution?

It should be possible to use a series of specially prepared test papers, in combination with a few chemical separations, to completely identify the components of a solution containing several cations and anions; devise such a series of test papers and work out a qualitative analytical scheme involving their use. (If you wish to perform a complete study, determine the sensitivity of your tests for each cation and anion.)

---

## Vapor Diffusion Methods in Qualitative and Quantitative Analysis

*See* HUGHES, H., *J. Chem. Educ.*, **28**, 195–197 (1951).

A small, shallow glass dish, not unlike a Petri dish, is used in this procedure. The mid-region of the interior of the dish consists of a central compartment bounded by a rim, lower than the outermost circumferential edge, and concentric with it. An indicating reagent is placed in this central compartment, and a reagent which will react with the substance to be analyzed and yield a volatile product is placed in the surrounding annular space. The substance to be analyzed is introduced into the annular compartment and the apparatus is covered with a flat glass plate. The time required for a change in color, the appearance of a precipitate, or other observable phenomenon in the central compartment can be used to calculate the quantity or concentration of unknown in the annular compartment. Prior measurements with a known solution are necessary.

Several variables must be controlled for precise results. These include temperature, method of adding the unknown, the manner of mixing the liquids in the annular compartment, the thickness of this liquid layer, and the intensity of radiant light falling upon the apparatus. The glass apparatus, called a "Conway unit," is not readily available; but a substitute suitable for most procedures can be turned from a half-inch thick piece of Plexiglas or other polymer. (Dimensions are given in the article.)

**Questions:**

Repeat the procedure described and determine the percentage of nitrogen in an impure ammonium salt.

Modify the procedure as necessary in order to determine the percentage of hypochlorite, chloride, sulfite, carbonate, or cyanide, in an appropriate sample.

Many inexpensive automotive antifreeze liquids contain methyl alcohol. Determine the composition of such an antifreeze.

Some disinfectants contain formaldehyde or phenol. Determine the composition of a disinfectant and compare your analysis with that indicated on the label.

Carry out the procedure described for the determination of nitrogen, or carry out a similar procedure for the determination of hypochlorite, chloride, or sulfite, and determine the limits of precision of your procedure.

Can the precision of this method be improved so that it is comparable to the precision obtainable from the more common methods of analysis?

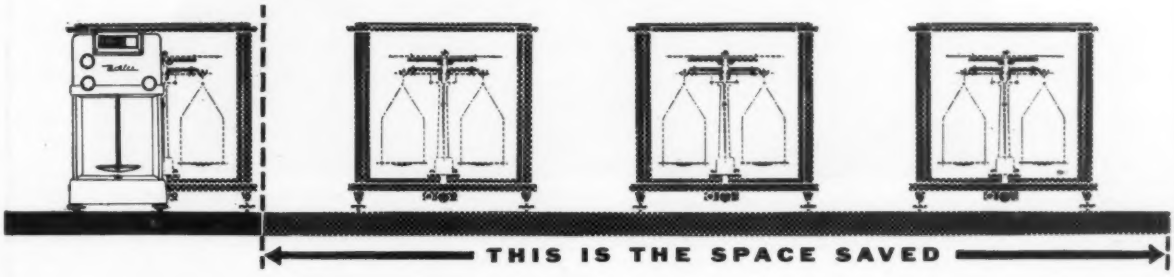
+ + +

ERRATUM: Dr. Gerald J. Cox, University of Pittsburgh School of Dentistry, points out the spelling error on page A263 of the April Chemical Projects. He passes on the advice he gives his students, "Do not knock the 'l' out of Hasselbalch."

$$X = \frac{\Sigma(\$ \text{ for balances})}{N \text{ students}}$$

The X in this formula stands for the amount of money per student spent on balances. This is your true cost. It is lowest on Mettler balances because of the savings in the number of balances needed and the space occupied by them. Furthermore, instructors and students use less time.

This diagram represents the space saving.




The diagram is based on the conservative assumption that one Mettler balance does the work of four equal-arm, undamped student balances.

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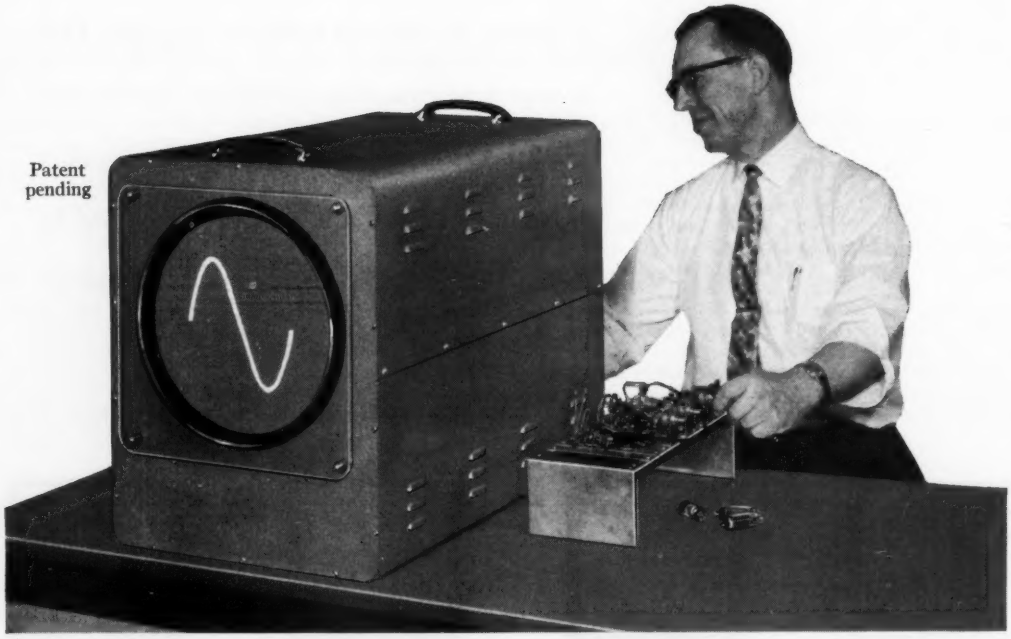

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# Chem Ed

## EDITORIALLY SPEAKING

The mail has been so interesting since the April "Editorially Speaking" appeared that at the risk of overworking a theme, we would like to share some of our letters with readers of this page. Correspondents registered a variety of reactions, from praise to condemnation, from contrition to righteous indignation. We apologize if the language was oversimplified; we intended no blanket indictments. Nor did we mean to knock chips off shoulders. We agree emphatically with one correspondent who restated the adage, "Education is knowing where to find it." What we tried to say was that science teachers should remember just this as an important part of the education they are giving their students.

We hope the following quotations do not appear out of the context the letter writers intended.

*A New England teacher:*

. . . This sounded like the plaintive wail of one who has helped build a Frankenstein and is now trying to duck the responsibility.

There is no time in the school day when I can discuss projects with my 119 students individually . . . I wish I could make the project optional, but experience has shown me that this arrangement produces no projects. Unfortunately I must demand projects from all to produce science projects from a few . . . I try to explain to them in class what a science project is. I spend a lot of time supervising, reading, organizing Science Fairs, all without financial compensation and with a minimum of peevish complaints, because I feel sure that a few of my 119 students are starting on the right road to being the scientists of tomorrow . . .

*A Pennsylvania teacher:*

. . . I must say I don't think you are being quite fair, either to teacher or student . . . If a teacher assigns a definite project, tells the student how to do it and where to find all the information, what earthly good is the project doing the student? Isn't the process of scouting around . . . part of producing the desired effect of teaching them something? . . . Most journals and books are written totally over their heads, and students learn early in life that industrial literature is written in nine-year-old English. Their letters to these companies are worded as best they know how for their limited knowledge in the field. Aren't you being a little cruel and snobbish? . . .

*A laboratory appliance supplier:*

I think that one comment of your beleaguered correspondent should be qualified . . . They're not stupid; they're just ignorant. These young people and their teachers have no idea where to get the information they want, or even what information they are looking for . . . They are not likely to find it in their school library or public library . . . The obvious non-stupid way out is to ask somebody. They write to any company they have ever heard of which may be connected with science . . . and, knowing nothing, they ask for everything.

You have hit straight at one of the solutions when you point out that science courses without science materials make no sense at all . . . It is a scared emphasis on science that puts teachers with no experience at work with no resources to make scientists out of youngsters with no interest.

. . . Ignorance and a sense of helplessness start most of these letters on their way to us—not stupidity, except well up the administrative scale with that superintendent, or teachers' college dean, or the state legislature, that dictates curriculum quantity with no regard for quality.

*An equipment manufacturer:*

We are in full agreement with your remarks . . . Our company like others in the chemical industry is most anxious to assist budding chemists and engineers in every way possible in supplying relevant and specific materials. We would hope that all teachers would look first through the excellent publication of the Manufacturing Chemists' Association (1825 Connecticut Ave., Washington 9, D. C.), "Guide to Education Aids Available from the Chemical Industry" before letting students request information.

*A Missouri teacher:*

Your editorial is very well put. Thanks for reminding us . . . I'm sure that I have been guilty of allowing my students to become a burden on many people.

*A Pennsylvania student:*

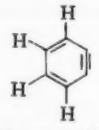
I would like to sincerely thank you for the information which you sent in answer to my request for material on the "History of Chemical Symbols." My project won First Prize . . .

We refrain from embellishing the points made in these lines and between them. Readers may find an interesting parallel in the comments by John Ciardi on page 8 of the *Saturday Review* for April 15, 1961. Reader, how would you answer ". . . such hopelessly hopeful casts as 'Please tell me what you think of William Butler Yeats. I am doing my term paper on him' "?

**Joseph F. Bunnett**
Brown University
Providence, Rhode Island

# The Chemistry of Benzyne

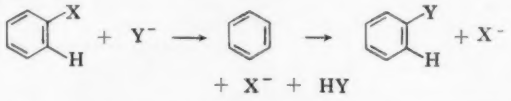
*Benzyne*, $C_6H_4$, is the parent of the family of *arynes*, not one of which has ever been isolated. Indeed, even physical detection of the short-lived



Benzyne (I)

$C_6H_4$ species was not reported until after the oral presentation of this paper in Cleveland. Notwithstanding, the chemistry of benzyne and its derivatives is a flourishing branch of organic chemistry, laden with interest for both the mechanisms and the synthetic chemist.

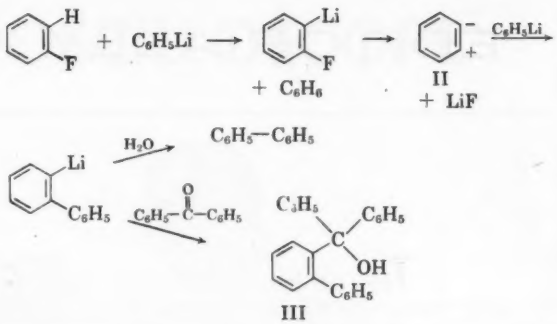
Arynes are usually generated by the action of a very strong base, such as potassium amide in ammonia or phenyllithium in ether, on an aryl halide. The base pulls out the elements of HX from adjacent positions. The aryne so formed has a short life, and



usually meets its end by adding a strong nucleophile (Y) and a proton to form Ar—Y. The over-all consequence is substitution, replacement of X by Y; this is known as the elimination-addition mechanism of aromatic nucleophilic substitution. Arynes may undergo other types of reaction too, as we shall see.

### The Benzyne Hypothesis

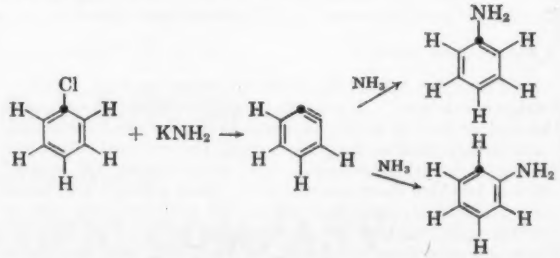
Aryne intermediates had been proposed, *ad hoc*, as early as 1902 (*1*), but stood in lonely isolation in the literature. Georg Wittig, in 1942 (*2*), was the first to advance the benzyne hypothesis (albeit in primitive form) with cogent experimental support. His key discovery was that the products from reaction of phenyllithium with fluorobenzene depend on the subsequent treatment of the reaction mixture. When water was added, biphenyl was the product; when benzophenone, *o*-biphenylyldiphenylcarbinol (III) was obtained. Wittig considered the unusual intermediate (II) to be permanently polarized in the sense shown.



He specifically rejected the symmetrical formula I. Very likely he would have recognized the symmetrical character of the intermediate were it not for an experimental mistake in his laboratory. The reactions of 2- and 3-fluoroanisole were described (*3*) as giving 2- and 3-methoxybiphenyl, respectively. In fact, as Huisgen and Rist (*4*) later demonstrated, both reactions give the *same* product, 3-methoxybiphenyl, attesting to a common intermediate, 3-methoxybenzyne:

IV

Another decade passed before John D. Roberts, in 1953 (*5*), published experiments which put the benzyne hypothesis on the road to general acceptance. In 1936, Francis W. Bergstrom had shown that the monohalobenzenes (except fluorobenzene) react with potassium amide in liquid ammonia to form aniline (*6*). Roberts showed that chlorobenzene-1-$^{14}$C gives nearly equal amounts of aniline-1-$^{14}$C and aniline-2-$^{14}$C. He suggested the mechanism:



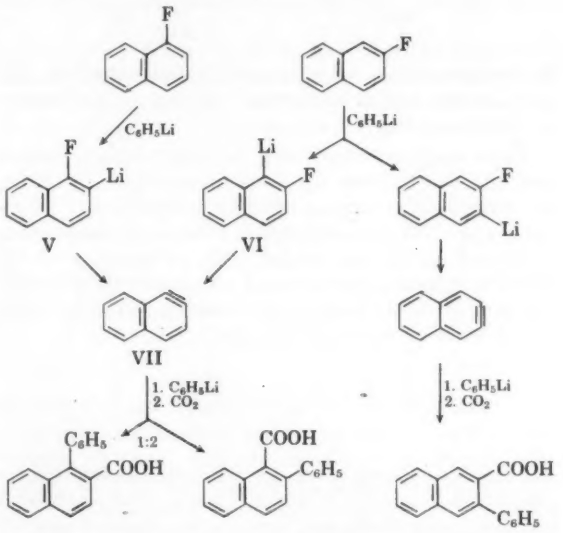
The slight difference from a 50:50 product ratio was of the magnitude and direction expected of a $^{12}C/^{14}C$ isotope effect. An alternative interpretation, that independent "rearranging" and "non-rearranging"

Based on a paper presented in the Symposium on New Outlooks in the Teaching of Organic Chemistry, Division of Chemical Education, at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

The author's research in aryne chemistry has received financial support from the Office of Ordnance Research, U. S. Army.

mechanisms were fortuitously matched in rate, was minimized by showing (*7*) that iodobenzene-1-$^{14}$C gave the same ratio of the two anilines; it is unlikely that the change from chlorine to iodine would affect rates of two independent reactions equally.

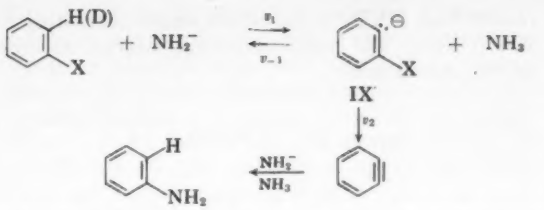
Roberts' 1953 communication was quickly followed by Rolf Huisgen's demonstration (*4*) that the reactions of 1- and 2-fluoronaphthalenes with phenyllithium, with subsequent carbonation, gave 2-phenyl-1-naphthoic acid and 1-phenyl-2-naphthoic acid *in the same 2:1 ratio.* (3-Phenyl-2-naphthoic acid was another product from 2 - fluoronaphthalene.) This showed the error of Wittig's presumption that the intermediate (II) was permanently polarized in a single sense. Huisgen's mechanism:




Strictly speaking, as he noted, an unlikely mobile equilibrium between V and VI would fit the facts as well as does the common intermediate, 1,2-naphthalyne (VII). Roberts' demonstration that phenyllithium and fluorobenzene-1-$^{14}$C formed virtually equal amounts of biphenyl-1-$^{14}$C and -2-$^{14}$C (*8*) was a further call for redefinition of the Wittig intermediate.

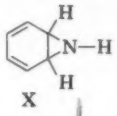
That halobenzenes lacking *ortho* hydrogens [e.g., 2-bromo-3-methylanisole (*9*)] are unreactive with sodium amide in ammonia was an important point in Roberts' original argument for the benzyne mechanism. The implication that *ortho* hydrogens are intimately involved was confirmed by hydrogen isotope experiments (*7*). When reaction of a mixture of ordinary bromobenzene and bromobenzene-2-d with $KNH_2$ was interrupted, the recovered unreacted bromobenzene was *richer* in deuterium than the original mixture. This shows that molecules with *ortho* deuterium react slower than ordinary bromobenzene. From the precise deuterium analyses and yields of halide ions, the ratio $k_H/k_D$ was reckoned to be 5.5, a magnitude characteristic of C—H bond breaking in the rate determining step.

Fluorobenzene-2-d quickly lost its deuterium when it was treated with $KNH_2$ in ammonia, but was otherwise unchanged (*10*). Chlorobenzene-2-d showed intermediate behavior (*7*). The results for the three halobenzenes were consistent with the scheme:



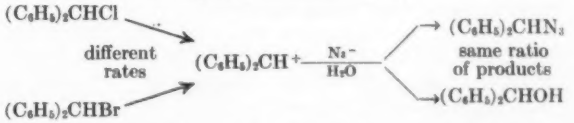

The intermediate phenyl anion (IX) may either capture a proton to regenerate halobenzene (rate $v_{-1}$) or lose halide ion to form benzyne (rate $v_2$). When X is fluorine, proton recapture predominates ($v_{-1} >> v_2$). When bromine, halide ion loss is the preferred reaction path ($v_2 >> v_{-1}$). When X is chlorine, $v_{-1}$ and $v_2$ are of comparable magnitude.

Roberts' carbon-isotope experiments spoke for a symmetrical intermediate, but the hydrogen-isotope results were necessary for the final exclusion of species such as X. Roberts' papers should be consulted for



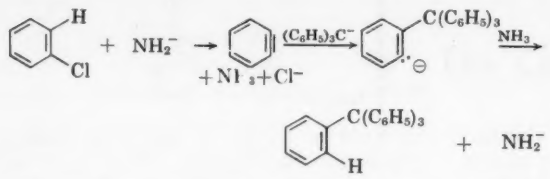

the detailed arguments (*7*). A last nail was driven in the coffin of the hypothesis of competing rearranging and non-rearranging reactions by demonstration (*11*) that iodobenzene-1-$^{14}$C-2,4,6-$d_3$ gives the same (47:53) ratio of aniline-1-$^{14}$C to -2-$^{14}$C as does iodobenzene-1-$^{14}$C. On that hypothesis the non-rearranging reaction, direct displacement of iodine by amide ion, should have been insensitive to change from protium to deuterium in the *ortho* position while the rearranging reaction (whatever its nature) should have been fully responsible for the retardation caused by *ortho*-deuteration; the proportion of aniline-1-$^{14}$C should therefore have increased sharply.

A classical model of proof for the existence of a discrete intermediate in a substitution reaction is the work of Hughes and Ingold which established the $S_N1$ mechanism of aliphatic substitution (*12*). Very important was evidence that rate-determination and product-determination occurred in separate steps. The proportioning of products between two or more alternatives was shown to be unaffected by changes in conditions which altered overall reaction rate. For example, diphenylmethyl chloride and bromide reacted at unequal rates in 90% aqueous acetone in the presence of sodium azide but gave the same ratio of diphenylmethyl azide to diphenylcarbinol (*13*).




It is most dramatic when the product-forming reagent is unable to generate the intermediate. No reaction occurs until an intermediate-generating reagent is introduced. In benzyne chemistry, such a case is the "reaction" of potassium triphenylmethide with chlorobenzene in liquid ammonia. As Bergstrom observed in 1936, without being able to offer an explanation, nothing happens until one adds $KNH_2$, of which a little bit is sufficient (*14*). The ensuing smooth reaction forms (principally) tetraphenylmethane. We now

realize that $KNH_2$ is the intermediate-generating and $K^+C(C_6H_5)_3^-$ the product-forming reagent, according to this mechanism:

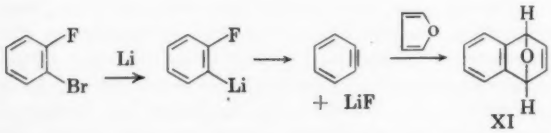


Amide ion is regenerated, and thus a tiny amount suffices to catalyze the reaction.

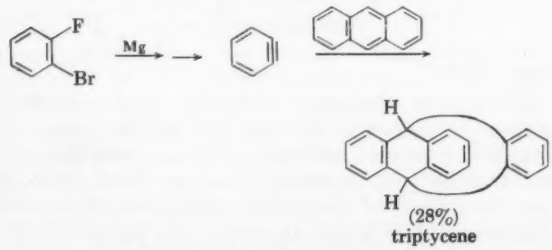
Similarly, the formation of diphenyl sulfide from bromobenzene and thiophenoxide ion (*15*) and the formation of biaryls from aryl halides and phenyllithium (*16*) are catalyzed by metal amides. The latter case has received detailed kinetic study (*17*).

Halonaphthalenes react with metal amides in the presence of piperidine to form mixtures of $\alpha$- and $\beta$-naphthylpiperidines (*18*). Six monohalonaphthalenes ($\alpha$- and $\beta$-, chloro-, bromo-, and iodo-) gave, on reaction with lithium piperidide and piperidine in ether, *the same mixture* of $^1/_3$ $\alpha$- and $^2/_3$ $\beta$-naphthylpiperidine (*19*). This is strong evidence for a common intermediate in all six reactions, namely, 1,2-naphthalyne (structure VII, below). Specifically, the fact that neither the position nor the identity of the halogen affects the partitioning of products shows that distinctions between the halogen-bearing and hydrogen-bearing positions are lost in the intermediate and that the halogen atom is either absent or relegated to such a subsidiary position as to have no appreciable effect on the intermediate's reactivity.

Benzyne, with its very reactive "triple bond," promised to be a good dienophile. Wittig (*20*) showed that *o*-bromofluorobenzene reacts with lithium metal in furan solution to form naphthalene-1,4-endoxide (XI) in 76% yield. The probable course of the reaction is:

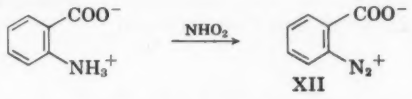


Similar reactions occur with other cyclic dienophiles; the reaction with anthracene is useful for preparation of the unique hydrocarbon, triptycene (*21*, *22*), which has the geometry of a three-blade water wheel, all three benzene rings being equivalent:



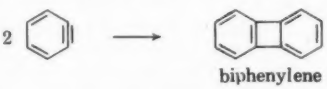
The fact that non-cyclic dienes do not give such adducts (*23*) speaks for a one-step mechanism, a true Diels-Alder reaction. Unlike most dienophiles, the short-lived benzyne intermediate cannot wait for open-chain dienes to assume the requisite *cis*-like conformation which is guaranteed in cyclic dienes.

Over all the foregoing, there hangs a shadow of uncertainty as to whether the aryne intermediates are truly free, or whether they may be loosely associated with metal cations or halogen anions. The long-sought goal of preparing benzyne in the absence of metal cations, halide ions or strong bases has recently been achieved by Martin Stiles (*24*). Benzenediazonium-2-carboxylate (XII), the zwitterionic diazonium salt from anthranilic acid, is isolable and stable (although explosive).



It decomposes on being heated in furan to form XI (55% yield) and in a benzene solution of anthracene to form triptycene.

These reactions imply that XII loses carbon dioxide and nitrogen to form the same intermediate, benzyne, as derived from organo-metallic compounds. Moreover, when XII is photolyzed in a vacuum, biphenylene is formed in the gas phase (*25*). Formation of biphenylene on decomposition of *o*-halophenyllithiums in solution, probably from simple dimerization of benzyne, has often been observed (*26*).



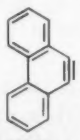
By the flash photolysis technique, it was noted that biphenylene formation lagged a few microseconds behind the activating flash, and that in the interval another species with a different spectrum held the stage. This is presumably benzyne, finally detected by direct physical measurement!

It must be acknowledged that, while benzyne can exist free in the gas phase, the species in solution may nevertheless be loosely complexed with solvent molecules, halide ions, or metal cations.

### Reactions of Arynes

Arynes are reactive in cyclo-addition (the Diels-Alder reactions and dimerization to biphenylene) and more notably in their capacity to add nucleophilic reagents. Since arynes are usually generated by basic reagents, themselves nucleophiles, the only nucleophiles whose additions to arynes have been observed are those which can compete successfully with the aryne-generating bases. These good competitors are anions with negative charge on carbon, nitrogen, or sulfur. Oxygen anions, such as $CH_3O^-$, are weak competitors.

Relative rates of addition to 9,10-phenanthryne



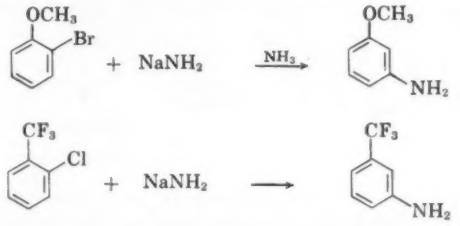
(XIII), measured by Huisgen (*27*), are given in Table

1. Greatest activity is shown by the sulfur anion reagent; next comes phenyllithium with negative charge on carbon, and then reagents with anionic nitrogen. No products from addition of oxygen anions were isolable.

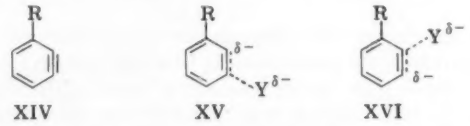
**Table 1. Relative Rates of Addition to 9,10-Phenanthryne (27) (in boiling diethyl ether)**

| Reagent | Relative rate |
|---|---|
| *n*-Butyllithium, $LiC_4H_9$ | 6300 |
| Lithium thiophenoxide, $LiSC_6H_5$ | 1700 |
| Phenyllithium, $LiC_6H_5$ | 1280 |
| Lithium piperidide, $LiNC_5H_{10}$ | 100 |
| Lithium phenylacetylide, $LiCCC_6H_5$ | 13 |
| Lithium dicyclohexylamide, $LiN(C_6H_{11})_2$ | 5 |
| Lithium phenoxide, $LiOC_6H_5$ | (0–3) |
| Lithium ethoxide, $LiOC_2H_5$ | (0–3) |

A notable achievement of the benzyne hypothesis was interpretation (*29*) of some curious reactions (*30*) observed in the 1940's by Bergstrom and by Henry Gilman, of which the following are typical:




In both, *ortho* reactants give *meta* products. The methoxy and trifluoromethyl groups, usually considered to have opposite electronic character (e.g., one is *o,p*-directing and the other *m*-directing in nitration), are both *meta* orienting. Roberts (*29*) proposed that the *inductive* effect of the substituent controlled the sense of addition to a 3-substituted benzyne (XIV).




XIV XV XVI

When the 3-substituent (R) was inductively electron-attracting, as both $OCH_3$ and $CF_3$ are, it would favor transition state XV for addition at the more remote position because part of the negative charge is localized on a carbon adjacent to the substituent. In the alternate transition state (XVI), both anionic centers are more distant from substituent R. Orientation is less specific when R is methyl (both *ortho* and *meta* products are obtained), which is consistent with this interpretation.

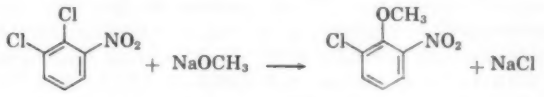
Steric factors also influence the direction of addition to arynes. The fact that 3-isopropylbenzyne (XIV, R = *i*-Pr) gives 96% of a *meta* product with lithium piperidide in piperidine, whereas 3-methylbenzyne gives $^2/_3$ *meta* and $^1/_3$ *ortho* (*31*), shows that the isopropyl group hinders attack at the position *ortho* to itself. Steric retardation of addition rate is also evident in Table 1 in the low reactivity of lithium dicyclohexylamide. This reagent has, surrounding the same type of nucleophilic center as in lithium piperidide, a great deal of bulkiness.

But withall, steric effects on rates of addition to arynes are comparatively small. Thus, reagents as different as phenyllithium, tert-butyllithium, sodium thiophenoxide, lithium piperidide and lithium diisobutylamide all add to 1,2-naphthalyne (VII) in the ratio $^1/_3$ $\alpha$ to $^2/_3$ $\beta$ (*15*, *28*). Only with lithium diisopropylamide (13% $\alpha$, 87% $\beta$) and lithium dicyclohexylamide (7% $\alpha$, 93% $\beta$) is steric interaction with the *peri*-hydrogen of VII, which retards $\alpha$-addition, in evidence.

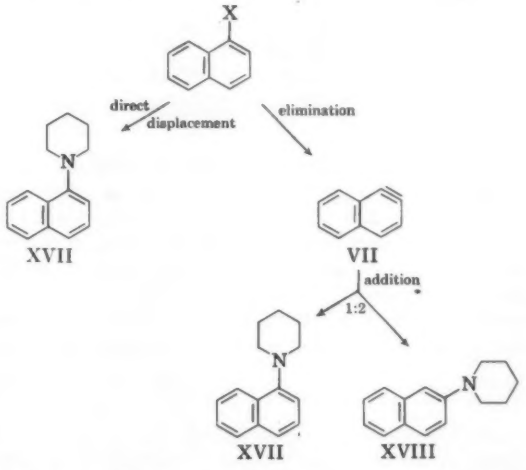
Furthermore, the fact that diverse reagents of the carbanion, sulfur anion and amide ion types all add about $^1/_3$ $\alpha$ and $^2/_3$ $\beta$ (above) indicates orientation in addition to be insensitive to the chemical type of the nucleophile.

### Boundaries of the Elimination-Addition Mechanism

Recognition of a new mechanism for aromatic nucleophilic substitution immediately raised questions as to its scope. Clearly it could not encompass all aromatic nucleophilic substitutions since many instances of displacement of groups flanked by two *ortho* substituents were known (*30*). Thus:




The most fruitful system for definition of the boundary between the more conventional (*30*, *32*) and the aryne mechanisms of substitution has involved reactions of 1-substituted naphthalenes with strong bases in

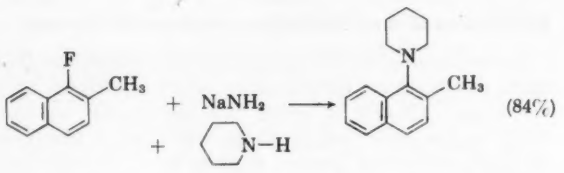



piperidine medium. The consequence of elimination-addition is formation of *two* products, XVII and XVIII in ratio 1:2, the major one representing rearrangement. The reactions of 1-chloro-, 1-bromo-, and 1-iodonaphthalenes with sodium amide in piperidine, reported by Brotherton and this author in 1956 (*18*), served to establish this ratio. In contrast, direct displacement forms a single unrearranged product, XVII.

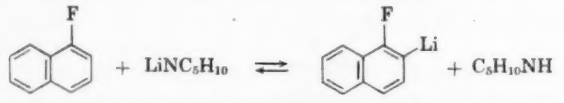
Direct displacement was evident in the high temperature reaction of 1-bromonaphthalene with piperidine (in the absence of sodium amide) and in the reactions of 1-naphthyl methyl sulfone, 1-naphthalenesulfonic acid (sodium salt) and 1-naphthyl phenyl ether with sodium amide in boiling piperidine, all of which

formed XVII but no XVIII (*18*, *33*). It thus became clear that a *strong* base (e.g., sodium amide) was necessary to generate 1,2-naphthalyne even from 1-bromonaphthalene, and that even in the presence of sodium amide the $-SO_2CH_3$, $-SO_3^-$ and $-OC_6H_5$ substituents resisted aryne formation.

1-Fluoronaphthalene gave, with sodium amide in piperidine, the unusual ratio of 60% XVII to 40% XVIII. This indicated competition between the two mechanisms: 40% direct displacement versus 60% elimination-addition. The reaction with 1-fluoro-2-methyl-naphthalene showed that direct displacement of fluorine could occur under the conditions involved (*18*).

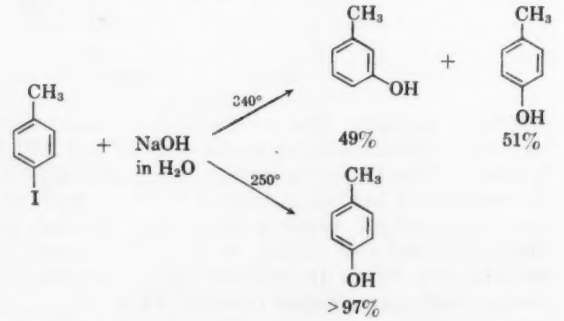



Huisgen's study of the reaction of 1-fluoronaphthalene with lithium piperidide in ether (*34*) showed the proportion of direct displacement to dwindle as the piperidine concentration decreased. With much piperidine the ratio of XVII to XVIII is 58:42 (as with $NaNH_2$ in piperidine), while in the absence of free piperidine it is 30:70 (indicating exclusive elimination-addition). Piperidine acts to reverse the initial metallation, and thereby to repress




elimination, giving direct displacement a better competitive position.

The high temperature reaction of aqueous sodium hydroxide with aryl halides often gives rearranged products indicative of an aryne mechanism (*35*). Thus, *p*-iodotoluene and NaOH at 340° give 49% of *m*-cresol and 51% of *p*-cresol. But *the same reactants at 250°* give only *p*-cresol. Elimination-addition no longer prevails at the lower temperature. Carbon-14 experiments indicate a large extent of elimination-addition



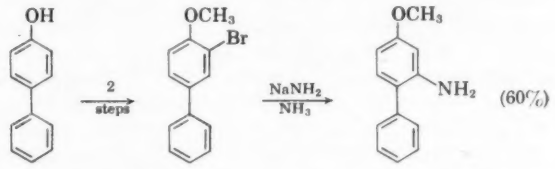

in the reaction of chlorobenzene with NaOH under the conditions of the Dow phenol process (*35*). This is benzyne chemistry on the tonnage scale! This mechanism also accounts for the by-products (e.g., 2-hydroxybiphenyl) formed in that process (*36*).

The borderline between the two mechanisms is by no means fully defined. Work to date shows that changes in the reagent, the group displaced, and the temperature can each affect its location.

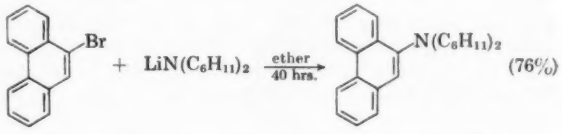
### Applications in Synthesis

To the synthetic chemist, the unusual characteristics of aryne chemistry and the frequent incidence of high yields offer great opportunities. The very fact that reactions via aryne intermediates do not obey the conventional rules means that they can be used to do things which more familiar methods cannot do. Yet exploration of synthetic applications has lagged. This is mainly because the field as a whole has been developed by mechanisms chemists to whom synthetic applications are of secondary interest.

The rearranging character of many substitutions by the elimination-addition mechanism offers a route to positional isomers otherwise difficult of access. A good example is the 2-amino-4-methoxybiphenyl synthesis of Bradsher, Brown and Leake (*37*):

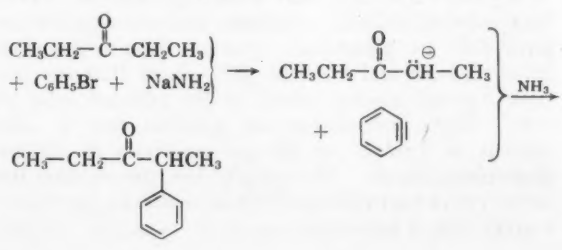



Even when rearrangement is not observable, an elimination-addition reaction may be the synthesis of choice. Thus 9-phenanthryldicyclohexylamine is easily prepared (*38*):



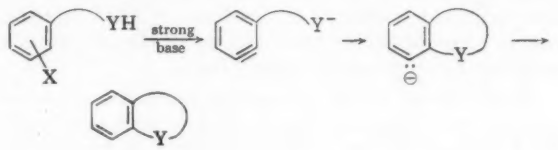

The most convenient though not always the best way to perform such aminations is to reflux the aryl halide with $NaNH_2$ in excess secondary amine (*40*). Reactions of aryl halides with aryllithiums catalyzed by lithium piperidide are a route to biaryls, of which a good deal is known from Huisgen's researches (*16*, *39*). but which has apparently not received specific attention as a synthetic method.

Carbanions derived from ketones (*41*), esters (*41*) and nitriles (*15*, *42*) may also be arylated. Malonic ester has been phenylated (51% yield) by bromobenzene and $NaNH_2$ in ammonia (*41*), in contradiction of textbook statements of the pre-benzyne era that this conversion is impossible. Phenylation of diethyl ketone by the same reagents gave a 62% yield of 2-phenyl-3-pentanone, a compound otherwise accessible



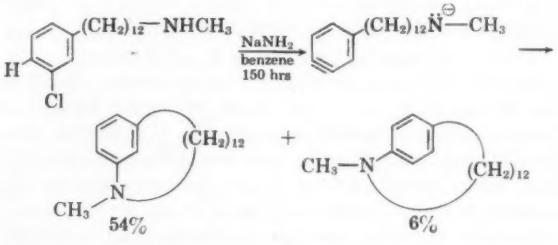
only by a multistep synthesis.

A synthetic application pregnant with potentialities is ring closure via aryne intermediates. Pioneering work has been done by Huisgen and co-workers (*43*) and by Hrutfiord and this author (*44*). The principle of such ring closures is to create an intermediate which has both an aryne "triple bond" and a strong nucleophile suitably located in a side-chain. The nucleophile adds intramolecularly to the aryne structure, and finally a proton is acquired. In general symbolism:



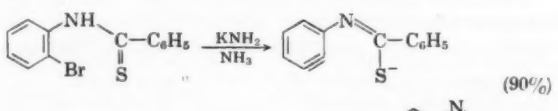
The German workers mainly investigated cases in which YH was a secondary amino group, with phenyllithium or lithium diethylamide (in ether) as the base. A representative ring closure was:

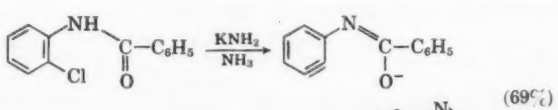
The same product was obtained from the *ortho* isomer, though in lower yield. Of the many additional examples studied, a particularly interesting one was:



Here, the nucleophile is at the end of a long side-chain and can reach across to add to *meta* and *para* positions.

Our work has concerned a more general selection of side-chain nucleophiles, with $KNH_2$ in ammonia as the base. The following ring closures are representative:

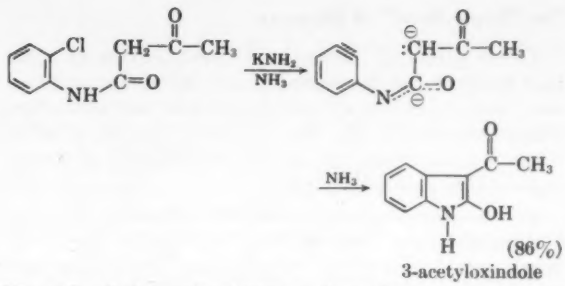




2-phenylbenzothiazole



2-phenylbenzoxazole



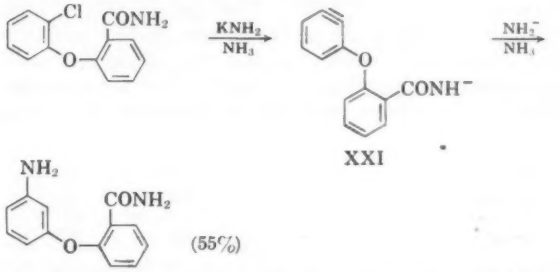
3-acetyloxindole

The side-chain nucleophiles in these three examples are sulfur, oxygen, and carbon anions, respectively.

Countless applications of this principle of ring closure can be visualized. In exploring some of these, we have however encountered limitations. Kato (*45*) found, for example, that phenylacet(*o*-chloro)anilide

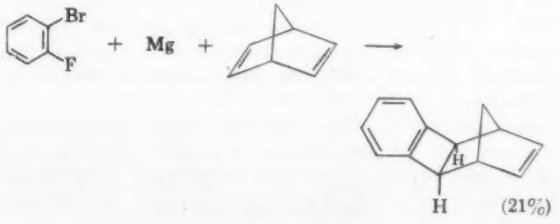
(XIX) could be recovered unchanged from treatment with $KNH_2$ in ammonia, although its N-methyl derivative underwent ring closure to 1-methyl-3-phenyloxindole in 91% yield. *o*-Chlorophenylacetamide (XX) also resisted aryne formation. The reason for this impressive unreactivity of certain aryl chlorides is apparently that protons are initially removed from the atom *alpha* to the aromatic ring, transforming that atom into an anionic center which shares its charge (through resonance) with ring carbon atoms. This decreases the acidity of ring hydrogens so that they are not attacked by amide ion.

Another difficulty is that the aryne intermediate is sometimes attacked by external amide ion, rather than by the side-chain nucleophile, forming a simple amination product as in this case (*45*):



In the preferred conformation of the intermediate (perhaps XXI), the $-CONH^-$ nucleophile is probably too far from the "triple bond" to compete effectively with amide ion.

Wittig's Diels-Alder reactions provide ready access to unusual structures. Another cycloaddition of synthetic interest is that of benzyne to bicycloheptadiene (*46*):

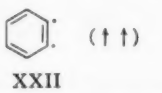


### The "Triple Bond" of Benzyne

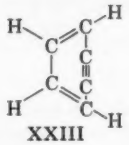
Three principal views have been advanced: (a) that benzyne has the same kind of triple bond as in an acetylene, involving *sp* hybridization of the two carbon atoms concerned; (b) that it has a special kind of triple bond between two $sp^2$-hybridized carbon atoms; and (c) that it is a diradical.

In a bookkeeping sense, benzyne is benzene less two hydrogen atoms. One electron from each of the C—H bonds sacrificed in this "transaction" is left on each carbon atom. The problem is: Do these two electrons interact to form a bond and, if so, how?

If their spins are parallel, the two electrons do not form a bond; one then has the diradical XXII. Benzyne shows no reactions characteristic of radicals, and alternative (c) is therefore dismissed.



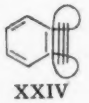
XXII



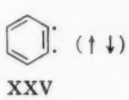
XXIII

An objection to alternative (a) is that the linear geometry of the acetylenic —C≡C— cannot be accommodated because the rest of the six-membered ring would be distorted too much (structure XXIII). It is however conceivable that some sort of compromise is reached, each part of the ring yielding its usual geometrical preference to some extent. This view has been advanced in responsible quarters (*7*, *47*). After all, if cyclopropene with its double bond in a three-membered ring can exist, why should not a species with an acetylenic bond in a six-membered ring be capable of transitory existence?

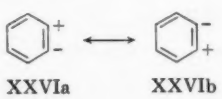
Alternative (b) is best represented in orbital symbolism (structure XXIV). The carbon atoms keep their $sp^2$ hybridization as in benzene, and the electron pair of interest is resident in the two $sp^2$ orbitals ordinarily used for bonding with hydrogen or substituents. These orbitals have their axes in the plane of the ring



XXIV



XXV



XXVIa XXVIb

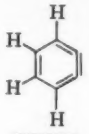
and overlap sideways to some extent, creating a weak bond. In valence-bond language, there is resonance between the "triple bond" structure I and the "double bond" structure XXV. The latter is *not* a diradical, because the spins of the two electrons are antiparallel. XXV may be thought of as a hybrid between the dipolar structures XXVIa and XXVIb.

The advantage of alternative (b) is that it maintains the normal benzene geometry and aromatic resonance. The "disadvantage" that sidewise overlap of $sp^2$ orbitals does not form a strong bond is actually in excellent accord with the high chemical reactivity of benzyne.

Alternative (b) has received some experimental support (*48*). Phenyllithium is a more active nucleophile than lithium piperidide in reaction with arynes but the ratio $k_{LiPh}/k_{LiNC_5H_{10}}$ varies, as follows: benzyne (I), 4.4; 1,2-naphthalyne (VII), 5.8; 9,10-phenanthryne (XIII), 12.8. The greater selectivity of 9,10-phenanthryne implies that it is a more stable molecule, more able to wait for the stronger nucleophile to come along, less obliged to react with the first one it encounters.

Structure XXIV gives a satisfying account of this order of aryne stability. Bond length measurements in the parent hydrocarbons tell us that carbon atoms 9 and 10 of phenanthrene are closer together than 1 and 2 of naphthalene which in turn are closer than any two adjacent carbons of benzene. Closer spacing should cause better sidewise overlap of the $sp^2$ orbitals and therefore a stronger "third" bond.

Whatever the nature of bonding, symbol I is now in general use. Worth noting is that it does not imply bond fixation in the aromatic system; a more complete notation would show resonance between I and the "cumulene" structure XXVII.



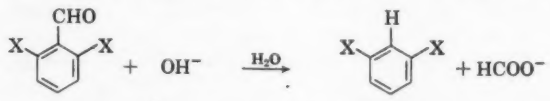
XXVII

### Phenyl Anion Chemistry

Arynes are usually generated by expelling halide ion from an *o*-halophenyl anion intermediate (e.g., IX) which either exists as such or in association with a metallic cation (via ion pairing or partially covalent bonding). A by-product of aryne research is some information about the chemistry of phenyl anions.

From preparative metallation experiments (*49*), rates of hydrogen isotope exchange under catalysis by strong bases (*10*) and rates of aryne formation from substituted bromobenzenes (*50*), it is known that formation of phenyl anion intermediates is remarkably fast when certain atoms or groups are *ortho* to the anionic center. Particularly helpful are the halogens, especially fluorine, and the methoxy and trifluoromethyl groups. The beneficial effect is severely reduced when these groups are removed to the *meta* position. For instance, fluorobenzene-3-d exchanges with $KNH_2$ in liquid ammonia some three powers of ten slower than fluorobenzene-2-d. The *para* isomer is slower yet.

The same influence is evident in the cleavage of 2,6-dihalobenzaldehydes by alkali; this reaction fails unless both *ortho* positions are occupied by halogen

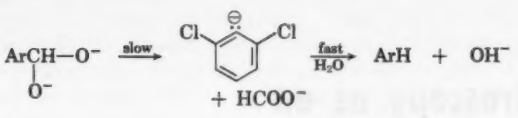


atoms (*51*). Nitro groups are also effective. A kinetic study (*52*) indicates the mechanism:

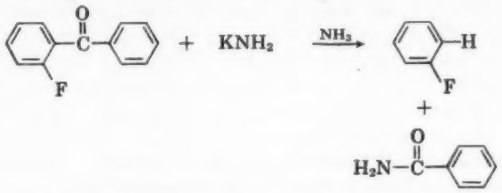
$$ArCHO + OH^- \rightleftarrows ArCH(OH)-O^- \quad \text{fast}$$

Ar = 2,6-dichlorophenyl

$$ArCH(OH)-O^- + OH^- \rightleftarrows ArCH(O^-)-O^- + H_2O \quad \text{fast}$$



Closely related is the cleavage of *o*-fluorobenzophenone by $KNH_2$ in ammonia (*53*):



*m*- and *p*-fluorobenzophenones are resistant to cleavage under identical conditions.

The stabilization of phenyl anions by *ortho* halogens, $OCH_3$ and $CF_3$, which is also responsible for *meta*-orientation in addition to 3-substituted benzynes (see above), is often attributed to inductive effects. Whatever the nature of the influence, it seems to be the same as governs basicity in substituted pyridines (which are isoelectronic with phenyl anions), since a good linear free energy correlation has been demonstrated (*50*) between substituent effects on aryne formation rates and on the basicities of pyridines (*54*).

## Conclusion

Benzyne chemistry is in a sense only eight years old. He is a robust lad. A lot of excitement has attended his growth, and those who have watched his antics are confident the excitement is far from over. His future prospects are bright; he will become a strong and influential member of the family.

Two recent reviews of aryne chemistry by Huisgen, one in German (*28*), the other in English (*39*), are essential reading for the serious student of this subject. Quite properly, they give a large share of attention to the abundant results from his own laboratory. One important topic slighted in the present paper is Huisgen's research on the kinetics of aryne formation. Two reviews by Roberts (*55*) and one by Wittig (*26*), although older, are also valuable.

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# NMR Spectroscopy as an Analytical Tool in Organic Chemistry

The massive impact of the use of infrared spectroscopy on the research methods of organic chemists has done much to condition us to the rapid acceptance of new physical methods. This has been demonstrated during the last seven years by the development of nuclear magnetic resonance (NMR) spectroscopy as a research tool of the organic chemist. Three reference texts appearing recently outline this development in a manner most useful to the organic chemist: the brief introduction by Roberts (*1*), the recent book of Jackman (*2*) and the more theoretical and detailed treatise of Pople, Schneider and Bernstein (*3*).

The commercial availability and widespread use of instrumentation for NMR spectroscopy has rendered an understanding of the technique indispensable to the modern organic chemistry student. The steadily increasing number of schools and research institutions sufficiently interested in the technique to undergo the rather substantial financial outlay necessary to set up an NMR laboratory bespeaks its tremendous usefulness in all fields of chemistry. This usefulness is particularly noteworthy in organic chemistry, where NMR threatens the primacy of infrared spectroscopy as an aid in structure determination. The two spectroscopic disciplines complement one another and, combined, are much more effective than either separately.

It is often desirable to introduce a class, such as an undergraduate class in qualitative organic analysis, to the use of NMR spectroscopy in a manner sufficiently qualitative to be covered in two or three lectures, yet detailed enough to permit an appreciation of the applicability of the technique in structure determination. I approach this presentation with the aim of simplifying, perhaps at the risk of over-simplifying, the theoretical concepts involved so that I can emphasize the practical aspects of interpretation essential to the student who will be using NMR spectroscopy as an analytical tool in his undergraduate or graduate research. As the student encounters in his own research spectra which are (in the simple view) anomalous, he will be encouraged to dig more deeply into the theoretical bases of the method in order to resolve these anomalies.

Fortunately the interpretation of NMR spectra is, in the simpler cases, much more straightforward than the interpretation of infrared spectra. It is often possible to make a complete analysis of a rather complex spectrum on inspection, making assignments for each peak.

One simplifying feature of NMR spectroscopy is that the area of the absorption peaks for a given set of protons is directly proportional, in a properly obtained spectrum, to the number of these protons. This is a tremendous help in the analysis of a spectrum.

Two factors must be considered in making such an analysis: the "chemical shift" (usually represented by $\delta$) (*4*) and the "spin-spin interactions" (expressed by a "coupling constant" $J$) of the various protons in the molecule. It is the purpose of this paper to review briefly and qualitatively the physical bases of NMR spectroscopy and to discuss the ways in which chemical shift and spin-spin interaction phenomena depend on molecular structure.

A proton in a static magnetic field may have two orientations with respect to this field. These two orientations differ in energy and transitions between them may be induced by radiation of this energy (the radiofrequency range for experimentally attainable fields). The equation

$$\nu = \gamma H_p$$

defines the relationship between the magnetic field, $H_p$, at the proton and the frequency, $\nu$, of the radiation required for resonance at this field, in terms of a proportionality constant, $\gamma$.

### The Chemical Shift

If the proton in question is surrounded by a spherical electron cloud, as in Figure 1, a field will be induced within this electron cloud opposing the applied field $H$. The magnitude of the induced field at the proton will be proportional to the magnitude of the applied field $H$ with a proportionality constant which we may call $\sigma$, a shielding constant. The term "shielding constant" refers to the fact that the diamagnetic induced field of the electron cloud shields the proton so that it does not experience the gross magnetic field $H$, but experiences this field reduced by an amount $\sigma H$ attributed to the induced field.

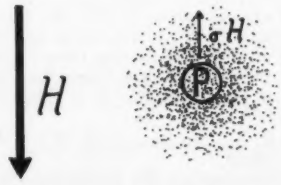



**Figure 1. Magnetic shielding of a proton in a spherical electron cloud.**

The chemical shift results from the fact that a given proton in an organic molecule in solution experiences an average magnetic field which is not the same as the gross field in which the sample is placed. Protons in

organic compounds are not bare protons but are embedded in clouds of electrons. They are therefore subject to the diamagnetic shielding mentioned above, the individual proton experiencing a magnetic field less than the applied field by an amount which is, as a first approximation, proportional to the electron density near the proton. As we shall see later, electrons more distant from the nucleus may have either a shielding or an unshielding effect depending upon the shape of the electron cloud and the geometry of the molecule.

Different protons in the same molecule may be in different average local fields as a result of different shielding. At a given frequency of irradiation, therefore, different values of the applied field $H$ will be necessary to bring each proton in turn into the field necessary for resonance; the more shielded the proton, the higher the necessary field.

The conditions for resonance for the various protons in a molecule (i.e., an NMR spectrum) could be defined in terms of values of the applied field, $H$, at a constant frequency, $\nu$, or in terms of the values of $\nu$ at a constant gross field, $H$. (Experimentally the field strength $H$ is the parameter which is varied, at constant $\nu$.) In practice neither of these alternatives is followed. Since the range of resonance conditions for the various types of protons in organic compounds is very small, compared to the absolute values of either frequency or magnetic field strength, such a procedure would require a 9-digit number to specify the value of $H$ (or $\nu$) for a given type of proton and only the last three digits would change as the type of proton changed in various organic molecules. It is therefore, as a matter of convenience, customary to express the conditions for resonance in terms of a difference (the chemical shift) in field strengths $H$ at constant frequency, $\nu$. This difference is between the field necessary for resonance for the type of proton in question and the resonance field for a type of proton in some arbitrarily chosen compound.

The magnitude of the chemical shift depends upon the magnitude of local magnetic fields induced by the gross field, $H$. Since the magnitude of the induced fields is proportional to the magnitude of $H$, the shielding is also proportional to $H$ and the chemical shift can conveniently be expressed as a fraction of $H$. The value of the chemical shift expressed as a fraction (dimensionless units) in this way is independent of the frequency at which the spectrum is recorded.

Most logically these shifts could be expressed with reference to the field necessary for resonance of the "bare" proton, in the absence of shielding electrons. In experimental practice more easily accessible standards are used, the protons of compounds having sharp resonance peaks which can be used as reference points. Among the compounds that have been used are cyclohexane, benzene, toluene, water, chloroform, methylene chloride and tetramethyl silane. Extensive tables of chemical shifts are available as aids in the interpretation of spectra using various of these compounds as reference points.

From the viewpoint of the organic chemist, one of the greatest difficulties in the application of published chemical shift data to experimental problems has been the failure of workers active in the field to agree on a single system for expressing chemical shifts. If we logically choose to use dimensionless units, expressing chemical shift values independent of frequency, we are still left with the problem of choosing a suitable arbitrary reference compound.

The use of a symmetrical, unreactive reference compound such as tetramethyl silane in the same solution as the compound of interest (an internal reference) helps to minimize solvent effects on chemical shift. Such solvent effects are a result of shielding arising from the bulk diamagnetic susceptibility of the solvent. Both sample and reference are subject to the same shielding from this source, if they are in the same solution, and the chemical shift between sample and reference peaks is independent of the solvent. Specific solvent interactions such as hydrogen bonding can, on the other hand, change the relative positions of these peaks. Tetramethyl silane enjoys the double advantage (as a reference compound) of symmetry, which reduces the possibility of such specific interactions with solvent, and of such highly shielded protons that its resonance peak occurs at such high field that it does not obscure any of the other peaks in a spectrum.

Tiers (*5*) has proposed a widely-used system for expressing chemical shifts based on the use of tetramethyl silane as an internal standard. In this system the value of the chemical shift (designated $\tau$) is expressed as a difference in parts per million from the resonance position for tetramethyl silane on a scale which assigns the value 10.00 to the resonance for tetramethyl silane.

$$\tau \text{ (in ppm)} = 10.00 - 10^6 (H_{\text{Me}_4\text{Si}} - H_{\text{observed}})/H_{\text{Me}_4\text{Si}}$$

Under this convention most chemical shift values fall in the range 0–10 and increasing values of $\tau$ parallel increasing values of the applied field, $H$, and increasing shielding.

If the diamagnetic chemical shift which we have discussed depends on electron density around a proton it is not surprising to find a general correlation between the chemical shift of a proton attached to a given carbon and the electronegativity of other groups attached to this carbon. Such a general correlation is easily discernible from the data presented in Figure 2.

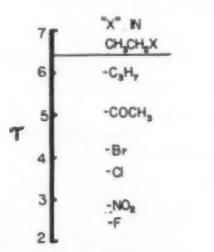



Figure 2. Methylene chemical shifts of $CH_3CH_2X$.

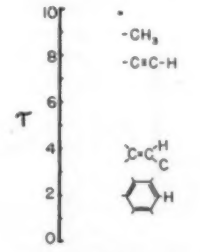



Figure 3. Chemical shifts and magnetic anisotropy.

The lack of generality for such a correlation may be seen from Figure 3. Here it can be seen that the chemical shift values do not follow in the order of electronegativity of the carbon to which the hydrogen is attached ($sp > sp^2 > sp^3$). Although the hydrogens of the methyl group ($sp^3$ hybridized carbon) are more shielded than the vinyl hydrogen ($sp^2$ hybridized carbon) as predicted from electronegativity considerations, the acetylenic hydrogen ($sp$ hybridization) has a chemical shift intermediate to the other two. A significant

difference is observed between olefinic and aromatic type protons which cannot easily be predicted on the basis of electronegativity considerations.

The source of difficulty can be seen when it is recognized that electron clouds not immediately surrounding the proton but in neighboring bonds are magnetically anisotropic; the magnitude of a magnetic field induced in these clouds varies with the orientation of the molecule with respect to the applied field, $H$. Thermal tumbling of the molecule will not, in general, average out the effects of these induced fields on the protons; and a net contribution, either shielding or unshielding, to the chemical shift may result.

The anomalously high shielding of the acetylenic hydrogen may be understood, for example, when the effect of the field induced in the cylindrical $\pi$-electron cloud of the C—C bond is considered. This should be greatest when the C—C axis is parallel to the applied field. The induced current in the electron cloud can then follow the cylindrical contours of the cloud, and the large induced field opposes the applied field in the region of space occupied by the proton. Molecules with other orientations have smaller induced fields so that the average effect on the protons of a tumbling molecule is a shielding one (Fig. 4).

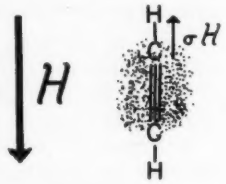



Figure 4. Magnetic anisotropy in acetylenes.

In the case of the protons of aromatic compounds such as benzene, on the other hand, the effect of magnetic anisotropy is an unshielding one. The maximum induced field in this case is obtained when the plane of the ring is perpendicular to the applied field. The current induced in the $\pi$-electron system may then flow around the ring, which acts as a superconductor. It can be seen from the representation of the lines of magnetic flux in Figure 5 that the effect of this rather large induced field at the proton is an unshielding one, the induced field reinforcing the applied field. The low value of $\tau$ for aromatic compounds has been well accounted for (*6*) on the basis of these ring currents.

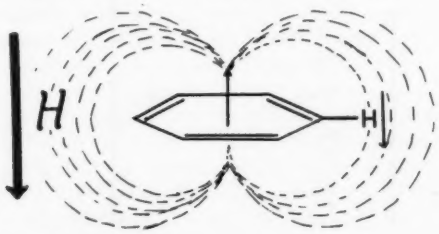



Figure 5. Magnetic anisotropy and ring current.

## Spin-Spin Interactions

A group of protons showing the same chemical shift may show not as a single sharp NMR peak but a multiplet structure of several peaks by virtue of interactions with other protons within the molecule.

For example, two protons on adjacent carbon atoms, as illustrated in Figure 6, may have their spins coupled in a manner not cancelled by the thermal motions of the molecule. This coupling involves the electrons in the

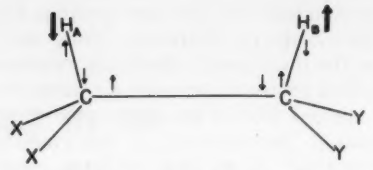



Figure 6. Spin-spin coupling of $H_A$ and $H_B$.

bonds joining $H_A$ and $H_B$. One explanation for such interactions proposes the transmission of the interaction through these bonds by virtue of the fact that the distribution of the two electrons in the C—$H_A$ bond is altered through the direct interaction between the spin of the proton $H_A$ (heavy arrow) and the spins of the electrons (light arrows). One of these electrons will have a favorable and one an unfavorable spin-spin interaction with $H_A$. The electron with the favorable interaction will tend to remain near $H_A$ leaving the other electron statistically nearer the carbon. This means that the electron spin at the end of the C—$H_A$ bond nearest carbon will not average zero. This provides the basis for a similar but smaller imbalance of electron spin in the C—C bond, which in turn is relayed through the C—$H_B$ electrons to $H_B$. It can be seen that the energy required for a magnetic transition of $H_B$ depends on the magnetic orientation of $H_A$ with respect to $H_B$. Since $H_A$ can have two possible orientations with spins $+ {}^1/_2$ and $- {}^1/_2$, the spectrum for $H_B$ will consist of a doublet. Similarly the spectrum for $H_A$ will consist of a doublet, the peak being "split" by spin-spin coupling with $H_B$. Such an interaction falls off rapidly with distance, splittings being observed, in general, for protons separated by three or fewer single bonds[1]. It will be noticed that the explanation advanced here for these interactions does not involve any reference to the applied field. The separation between peaks in a multiplet structure is, in contrast to separations attributable to chemical shifts, independent of the magnitude of the applied field. These separations are expressed in terms of a spin-spin coupling constant, $J$, which has the dimensions of energy and is most conveniently expressed in cycles per second.

In the simple case the chemical shift is equal to the distance between the two multiplet centers. This is true only if the chemical shift between $H_A$ and $H_B$ ($\tau_A - \tau_B$)—which may be expressed in frequency units at a given irradiation frequency, $\nu_0$—is large compared with $J$ (i.e., $10^{-6}(\tau_A - \tau_B)\nu_0 >> J$).

In Figure 7 we see the effect on the $H_A$-$H_B$ spectrum of varying the magnitude of the chemical shift relative to the magnitude of $J$. As the chemical shift becomes relatively smaller the relative intensities of the two peaks within a doublet change, the outer peak in each doublet becoming less intense.

At the limit where the chemical shift is zero these outer peaks disappear completely and $H_A$ and $H_B$ behave as a unit, showing only one peak with an area appropriate to two protons. As this limit is approached the separation between the centers of these increasingly unsymmetrical doublets becomes larger than the true

[1] Recent reports (*14*) of the observation of significant spin-spin interactions over four or five single bonds represent relatively rare cases. The usual practical limit for such interactions is three single bonds.

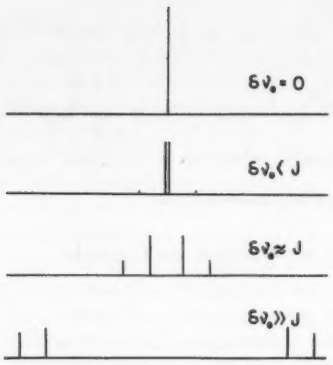



Figure 7. The effect of variation of the relative magnitudes of the coupling constant, $J$, and the chemical shift, $\delta\nu_0$.

chemical shift, approaching $J$ rather than zero as a limit. This typical pattern of intensities can be useful in interpreting spectra since the high intensity side of an unsymmetrical multiplet will always be on the same side of the multiplet as the peaks for the group of protons responsible for the spin-spin splitting. The separations between the peaks within one multiplet will be the same as the separations within the other, both being equal to $J$. This fact is also useful in determining which two multiplets result from groups of protons near enough to each other to interact significantly.

A third and most important factor in the interpretation of spin-spin coupling phenomena lies in a consideration of the multiplicity of the peaks. The interpretation of the more complex cases is similar to that discussed above. If instead of $H_A$ we have $n$ chemically equivalent protons all identically situated with respect to $H_B$, then $n + 1$ alignments of these protons are possible and the $H_B$ absorption will appear as a multiplet of $n + 1$ peaks.

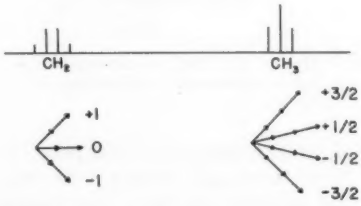
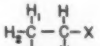



Figure 8. Multiplet structure for an ethyl group with the chemical shift large compared with $J$.

As an example we might consider a typical spectrum for an ethyl group, X—$CH_2$—$CH_3$, in Figure 8. The two protons of the methylene group are identical and, as a unit, can assume three orientations with spins $+1$, 0 and $-1$. The spectrum of the methyl peak will, therefore, consist of a triplet. The triplet is not symmetrical but has the peak nearest the methylene absorption more intense than the peak farthest away. The methylene absorption is by similar argument expected to be a similarly unsymmetrical quartet. The relative areas of the two multiplets are found to fall in the expected ratio methylene/methyl = $^2/_3$.

When the chemical shift is large with respect to $J$ we may use a statistical argument to predict the relative areas of the members of a multiplet. For example, the quartet corresponding to the methylene protons in an ethyl group should have peaks with areas which fall in the ratio 1:3:3:1 when the chemical shift is much larger than $J$. This can be predicted from a simple consideration of the number of ways a given total spin of the methyl proton group can be obtained (Fig. 9).

If the chemical shift approaches $J$ in magnitude, not only do difficulties arise with respect to the relative areas of the peaks within the multiplet, but also extra peaks not predicted by this simple treatment will appear as other magnetic transitions involving both groups of protons become more probable. For example a molecule with two identical protons interacting with a third would be expected to have a spectrum of five peaks, a triplet and a doublet, in the simple case. As the chemical shift approaches $J$ in magnitude, however, up to nine peaks are observed. It is obvious that the simple treatment is applicable only in the cases where there are simplifying factors. Fortunately these cases are frequently encountered.




| PROTON $H_1$ | PROTON $H_2$ | PROTON $H_3$ | TOTAL SPIN | STATISTICAL WEIGHT |
|---|---|---|---|---|
| + | + | + | +3/2 | 1 |
| + | − | + | | |
| + | + | − | +1/2 | 3 |
| − | + | + | | |
| + | − | − | | |
| − | + | − | −1/2 | 3 |
| − | − | + | | |
| − | − | − | −3/2 | 1 |

Figure 9. Statistical prediction of areas of multiplet peaks when the chemical shift is much larger than $J$.

The size of the coupling constant, $J$, depends not only on the number of bonds joining the two protons but on the nature and geometrical disposition of these bonds. In the case of protons on adjacent carbon atoms, for example, the value of $J$ is found to vary with the value of the dihedral angle between the two H—C—C planes in a manner predicted from theoretical calculations (*7*). The calculated values of $J$ are fit by the following functions of $\phi$, the dihedral angle

$$J = 8.5\cos^2\phi - 0.28 \text{ (cps) (from } 0 \text{ to } 90^\circ)$$
$$J = 9.5\cos^2\phi - 0.28 \text{ (cps) (from } 90 \text{ to } 180^\circ)$$

| *Dihedral Angle* | $J$ |
|---|---|
| 0 | 8.2 |
| 30 | 6.0 |
| 60 | 1.7 |
| 90 | −0.28 |
| 120 | 2.2 |
| 150 | 6.9 |
| 180 | 9.2 |

This dependence of $J$ on dihedral angle has been used in structure work, with particular success in studies of stereochemical relationships in cyclic sugars (*8*).

For the magnetic transitions with which we are concerned the transition times are sufficiently long that changes such as thermal tumbling, internal rotations about C—C bonds, etc., which require less time than $10^{-1}$–$10^{-2}$ seconds, are seen only as an average. For

this reason the three protons of the methyl group, for example, are equally coupled to the methylene protons in an ethyl group. Although at any instant of time the dihedral angles will differ for the three methyl protons, rotation about the C—C bond is so rapid that only the single average value of $J$ is observed.

The two protons of a methylene group are coupled to one another with a $J$ which has been shown (*9*) to be a function of the H—C—H angle. The theoretically calculated dependence on angle, Figure 10, has been confirmed by experiment in a number of molecules in which the H—C—H angle is known.

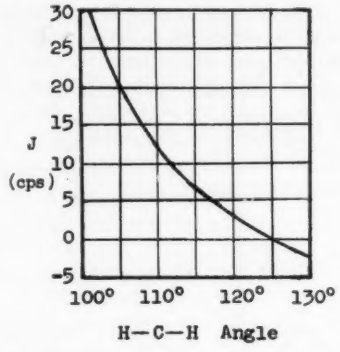



Figure 10. Variation of $J$ with bond angle.

If the chemical shift is zero between the two protons of a methylene group, only a single peak is observed (in the absence of other protons near enough to interact). When the methylene is a part of a ring, however, the two protons may not be chemically equivalent and, in the absence of other interactions, may give a spectrum consisting of two doublets. This can also occur in an acyclic case where there is free-rotation of the methylene group, if the methylene group is near a center of assymmetry in the molecule. In such a case the two protons may be magnetically non-equivalent and give the typical 4-peak spectrum characteristic of two dissimilar protons. Figure 11 shows a spectrum of this sort (*10*). The arrow points out the four peaks ascribed to the methylene hydrogens of the benzyl group which are non-equivalent by virtue of the assymmetry around the adjacent carbon.

The magnitude of $J$ has been most useful in determining stereochemical relationships in olefins. Protons located *cis* to one another on a double bond are less strongly coupled (usually $J$ = 8–11) than protons with a *trans* relation ($J$ = 17–19, both $J$'s expressed in cps).

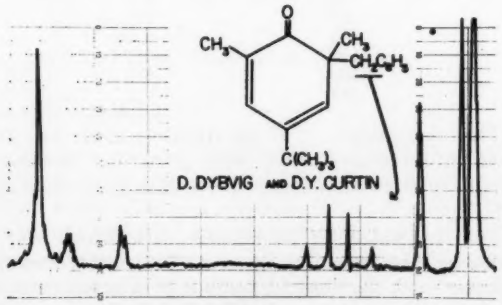



Figure 11. Magnetic non-equivalence resulting from molecular asymmetry.

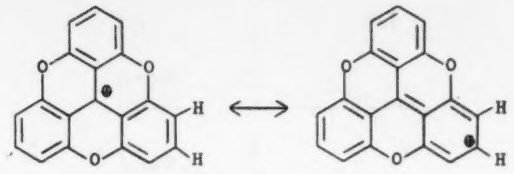



Figure 12. The sesquixanthylium ion.

### Application of Theory to an Example

To illustrate the factors involved in the interpretation of a typical spectrum of a new organic compound, let us examine the spectrum of a triarylmethyl carbonium ion, Figure 12, recently obtained in these laboratories (*11*), which can be called the sesquixanthylium ion.

Each ring contains two equivalent *meta*-hydrogens ($H_m$) and one *para*-hydrogen ($H_p$). The $H_m$ protons are identically situated with respect to $H_p$, making the $H_p$ spectrum a triplet. The $H_m$ spectrum is a doublet by virtue of interaction with the single $H_p$ proton. Interaction between protons on different rings is apparently too small to be observed. The coupling constant, $J$, is approximately 8.6 cps, a value within the range of those previously observed (*12*) for aromatic protons situated *ortho* to one another. The spectrum (Fig. 13) was obtained on a solution of the carbinol in trifluoroacetic acid.

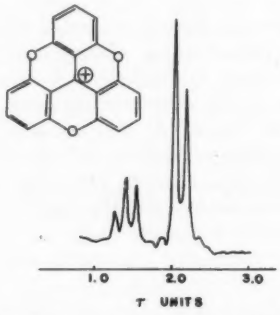



Figure 13. The sesquixanthylium ion in trifluoroacetic acid solution at 60 mc.

It was of further interest to compare the chemical shift for these hydrogen atoms with the chemical shift for the protons of more conventional triarylmethyl carbonium ions. The unique coplanarity of the sesquixanthylium ion allows a maximum resonance distribution of positive charge to the *ortho* and *para* positions of the aromatic rings. Electronegativity considerations would therefore lead us to predict a lower shielding for these hydrogens than would be observed for triarylmethyl carbonium ions in which the aryl rings are twisted from the plane of the molecule to relieve steric interactions. A suitable model compound for comparison was available to us (*11*) in the tri(2,6-dimethoxyphenyl)methyl carbinol, which also dissolves in trifluoroacetic acid to give a carbonium ion. This molecule gives a spectrum for the aromatic protons very similar in form to the spectrum of the sesquixanthylium ion but at higher field, the *para*-protons absorbing at 2.40 $\tau$ (rather than 1.54 $\tau$) and the *meta*-protons absorbing at 3.46 $\tau$ (rather than 2.22 $\tau$, as in the sesquixanthylium ion). This is the order of

chemical shifts which would be predicted from the consideration of positive charge density on the aromatic rings since the second ion must have its aromatic rings twisted out of the plane of the molecule by interactions between methoxyl groups.

Another factor must be considered, however, which turns out to work in the same direction as the charge distribution, namely ring current. The protons in the sesquixanthylium ion find themselves in the unshielding field of more than one ring. On the other hand twisting the rings as they must be twisted in this model ion, tri(2,6-dimethoxyphenyl)methyl carbonium ion, may place some of the aromatic protons within the shielding field of neighboring rings. This factor would also work to lower the resonance positions for the protons of the planar ion relative to those of the model. It is impossible to say which of these two factors is of greatest importance here without resort to tedious and uncertain calculations.

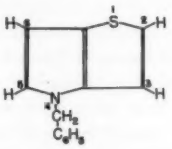


Figure 14. A Spin-spin coupling constant of 1.3 cps is observed between protons at positions 2 and 5

The transmission of spin-spin interactions through $\pi$-bond systems can cause an observable splitting over more than the three bonds considered a practical limit in saturated systems. In one case, the compound shown in Figure 14, a $J$ of approximately 1.3 cps is found (*13*) to couple protons (at positions 2 and 5) through at least seven bonds. Coupling through this many bonds is usually not large enough to be observed, however.

## Conclusion

If the simplifying conditions mentioned earlier (namely chemical shift $>> J$ and all protons in one group magnetically identical) are not met, or if large molecules with many types of protons are studied, the detailed interpretation of NMR spectra may become quite difficult. It is surprising, however, how the spectrum of almost any compound can impart some knowledge of its structure when interpreted on the basis of a knowledge of NMR spectroscopy no more detailed than that outlined here. The "anomalies" observed in spectra obtained from research samples provide the most effective possible goad to encourage the chemist to examine the theory pertaining to the more complicated cases.

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## Taste Tells!

The immediate application of large quantities of water is the standard and well-known treatment when acid is spilled on the skin. Most students who have had such a mishap will wash off the acid at once, then come to the instructor with the question, "Have I washed this enough?" A simple answer is, "Taste it and see." A taste test usually results in an immediate return to the sink for further washing, and the student need not consult the instructor again. This test is not only easily made and easily understood by the student, but it also illustrates a bit of chemical information that he should already have. Needless to say, the test should be made only *after* a preliminary washing.

The procedure described here is so simple and so easily carried out that it surely must already be in use by a large number of chemists. The frequency of the need for the test, however, makes it seem worth calling to the attention of all chemistry teachers.


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# The Uses and Abuses of Bond Energies

In the teaching of physical chemistry, the concept of "bond energy" is usually introduced during the discussion of thermochemistry, as a means of estimating heats of reaction (*1*, *2*). In this connection, the student may encounter statements such as, "In discussions of structure, thermodynamics, and chemical kinetics, it is often necessary to have some quantitative information about the strength of a certain chemical bond" (*1*); or he may find a table of bond energies with the heading, "Heats of Dissociation of Bonds" or "$\Delta H$ of Bond Dissociation" (*2*). Unless clarifying comments are added by the instructor, the student will have been misled in reading these items, or at best, confused. Among other difficulties, he does not realize that the bond energy which is of the most use in thermochemistry is usually different both in character and in numerical magnitude from that used in chemical kinetics; and he does not know that the heat of dissociation of a bond ordinarily has a numerical value which may be many kilocalories/mole larger or smaller than the bond energy used in thermochemical estimates. He may also be bothered by discrepancies in numerical values of bond energies for the same bond found in different texts, if he compares them. It is a rare student indeed who can ferret out an uncertainty in the heat of sublimation of carbon as the principal cause of the differences, without at least some word from the texts concerning this point.

Somewhat later the student may find bond energies being used in treating bonding and molecular structure (*3–7*), in further discussions of thermochemistry (*8–10*) in estimating the performance of rocket propellants (*11*), or in chemical kinetics and free radical chemistry (*12*, *13*). In several of these works he will find adequate comments on the concept of bond energy; if he looks further, he will obtain a clear understanding of the subject by reading Cottrell's book (*14*) and the articles by Szwarc (*15*) and by Szwarc and Evans (*16*). Once this has been accomplished, he will wish that he had read parts of the book by Cottrell much earlier, even at the elementary physical chemistry level. He will also wish that there were less ambiguity in the terminology used in discussing bond energies. During the examination of the references cited, a bewildering array of terms will have been encountered: "bond energy," "bond strength," "the strength of a certain chemical bond," "the energy necessary to break the bond," "a definite number of calories for each bond broken (or formed)," "heat of dissociation of a bond," "normal covalent single-bond energy," "average amount of energy required to break a particular bond in a molecule and separate the resulting (fragments)," "mean bond energy," "resonance energy," "the average amount (of energy) required to break all the bonds," "bond-dissociation energy," and "bond energy term," among others. Not only is the variety of terms a possible source of confusion, but worse, the same term is sometimes used to mean different things by different authors. For example, although "mean bond energy" and "bond-dissociation energy" are never considered to be synonymous, "bond energy" is used by Semenov (in translation) (*12*) to signify the bond-dissociation energy, by most of the others to signify the mean bond energy, and by Penner (*11*) to signify both (but with some explanatory remarks). The term "bond strength" is synonymous with "(mean) bond energy" according to Moore (*1*), whereas Glasstone (*6*), Remick (*7*), and Trotman-Dickenson (*13*) make it very clear that they consider it synonymous with "bond-dissociation energy." Cottrell (*14*) considers "bond strength" to be a general term encompassing several characteristics of bonds.

The plea of the present communication is twofold: one, that the concepts of bond energy and bond-dissociation energy be presented to undergraduate physical chemistry and organic chemistry students, and in enough detail that some real understanding results; and two, that the terminology be made unambiguous, insofar as this is possible.

It would be our preference to define "bond energy" as the contribution of the bond between a particular pair of atoms A—B in a molecule to the total binding energy present in the molecule. Its symbol is $E$(A—B). More qualitatively, it might be defined as the strength of the bond as it exists in the molecule, following Walsh (*17*). However, this introduces the ambiguous term "strength" into the definition, so that except for general conceptual purposes, perhaps, the first definition is preferable. It permits precise values of bond energies (usually at 298°K) to be assigned in diatomic molecules and in molecules of the type $AB_n$, when all A—B bonds are identical. In diatomic molecules, the bond energy is the heat of dissociation of the molecule, and in $AB_n$ molecules it is $(1/n)$ times the heat of atomization into A + $n$ B, with the atoms in their ground states. In polyatomic molecules other than $AB_n$,

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The drawing on the cover is a schematic representation of two atomization processes for methane, demonstrating the distinction between bond-dissociation energy and bond energy. Top: stepwise atomization; bottom, simultaneous atomization.

containing a variety of bonds, it is not possible to make precise assignments of bond energies. One must arbitrarily divide the heat of atomization into reasonable contributions from the several bonds. Where a series of similar molecules can be examined, as for example the paraffin hydrocarbons, $E$(C—H) and $E$(C—C) may be assigned constant values in such a way as to reproduce as well as possible the heats of atomization of the entire series. $E$'s for other bonds can then be deduced by obvious extension of the method. Certainly for making approximate thermochemical calculations, this is the best approach. From the previous definition of bond energy it is seen that $E$ values assigned in this manner are *average* bond energies, and their numerical values will depend upon the compounds selected for use in the assignment process.

More refined thermochemical estimates may sometimes be achieved by discarding the artificially enforced constancy of the average $E$'s, and instead insisting upon a "true" $E$; for example, the $E$(C—H) in methane might be chosen as the true value. If ethane were then taken as the standard for $E$(C—C), there would result a series of $E$ values for C—H bonds in other molecules, or one might compute an average $E$ for secondary and tertiary C—H bonds; or equally well, one could attribute differences to C—C bonds. In efforts to resolve the ambiguities inherent in such procedures, many attempts have been made to correlate bond energies with structural features of molecules, such as bond lengths. To the same general end, various mathematical definitions of bond energy have been put forward. Cottrell reviews these in detail. They are interesting and helpful, but not for undergraduate teaching and not for quick thermochemical computations. For these purposes one should rely upon average bond energies.

"Bond-dissociation energy" as a physical concept has a great advantage over "bond energy" in that it can be precisely defined, and because it is susceptible to direct experimental determination. It is the difference in enthalpy between the parent molecule and the two fragments produced when a bond is broken. The molecule and the fragments are all taken to be ideal gases and to be in their equilibrium configurations. The symbol given to the bond-dissociation energy is $D$, and the reference temperature is usually 0°K, but often 298°K. 298°K values are generally less than 1 kcal/mole larger than 0°K values. If 0°K is the choice, then even for diatomic molecules there will ordinarily be a small difference between the bond-dissociation energy and the bond energy because 298°K is the usual reference temperature for bond energies. In polyatomic molecules, the bond-dissociation energies will differ even at 298°K from the usual (298°K) bond energy values, aside from an occasional coincidence.

This is illustrated on the cover which shows schematically the two conceptions of the atomization process in methane at 298°K, leading to different values for $E$(C—H) and the four $D$(C—H)'s. There is still some uncertainty about details of the middle two stages of the atomization by steps, but in any event the sequence illustrates the point at hand. We begin, of course, with the tetrahedral $CH_4$ molecule. In the first step a hydrogen dissociation occurs and the $CH_3$ group becomes planar or nearly so. The hybridization shifts from $sp^3$ to $sp^2$ (for a planar $CH_3$), so that all the C—H bonds undergo some change in the process, not just the one broken. In the second step another hydrogen dissociates and the $CH_2$ group becomes linear.[1] The hybridization changes from $sp^2$ to $sp$. Again, all the C—H bonds have been affected. The third step breaks off a hydrogen from the $CH_2$ radical and the hybridization changes from $sp$ to a pure $p$ bond. Finally, this bond breaks and leaves the carbon atom in its ground state. It would be astonishing if the enthalpy requirements for these four steps were similar, in view of the gross electronic changes that occur and the changes in atom-atom repulsions, and indeed the requirements are very different. In the computation of the $E$(C—H), on the other hand, the process is envisioned as a simultaneous stretching of all four C—H bonds to infinite length while maintaining the geometry, but letting the carbon atom that results revert from its valence state to the ground state. Thus the total enthalpy requirements of the two processes are equal. One gains simplicity in the second process but loses knowledge of detail.

Despite their intrinsic advantages, bond-dissociation energies have not been used nearly as much as bond energies for estimating thermochemical quantities because (1) they are generally difficult to measure; (2) they are sensitive to the intra-molecular environment, so that one cannot readily formulate "bond additivity" rules for them of the sort implied (by definition) in the use of bond energies; (3) when dealing with reactions involving stable reactant and product molecules—i.e., no free radicals—the use of bond energies has been fruitful and of adequate accuracy for most purposes; and (4) if all the necessary bond-dissociation energy data were available for a reaction, there would be no need for making a thermochemical estimate, since the required information would already be known!

If one is interested in the thermochemistry or the chemical kinetics of reactions involving atoms or free radicals, the use of bond energies derived from the thermochemistry of stable molecules (in other words, typical bond energies) will produce serious errors. As an example, suppose the heat of formation of OH to be needed for some purpose. The bond energy of OH (equal to half the heat of atomization of water vapor) is 110 kcal. If the equation, $^1/_2H_2 + {}^1/_2O_2 \rightarrow OH$ is written, and the heats of atomization at 298°K are appropriately added and subtracted, the $\Delta H°_{298}$ of the reaction is found to be +1 kcal, which is thus the computed heat of formation of OH. Now the bond-dissociation energy of OH, although a bit uncertain, is probably about 103 kcal. If this figure is used instead of 110, obviously the resulting $\Delta H_f°$ of OH at 298°K will be 8 kcal instead of 1 kcal. A second example is CH. Using an $E$(C—H) from methane (99 kcal) to estimate the heat of formation of CH yields a value around 124 kcal, whereas the 298°K bond-dissociation energy of CH leads to a figure more like 142 kcal.

In chemical kinetics it is often important to make an

[1] Linearity of $CH_2$ is assumed for purposes of illustration. The precise shape is not yet established, but linearity is probable.

estimate of the activation energy of a reaction. Returning to the case of OH, consider the unimolecular decomposition of $H_2O_2$ into two OH radicals. If no activation energy is required for the radical recombination reaction, then the activation energy for the decomposition equals the O—O bond dissociation energy. The erroneous figure of +1 kcal for the heat of formation of OH leads to an O—O dissociation energy of 34 kcal, while the more nearly correct figure of +8 kcal produces 48 kcal as the result. These two activation energies yield predicted decomposition rate constants at 1000°K that differ by a factor of about 1000.

A second example may be cited that shows simultaneously the significance of using the correct energies in a thermal calculation and also in a kinetic estimate. The reaction, $H + C_2H_2 \rightarrow H_2 + C_2H$ is a hydrogen abstraction reaction which, if exothermic, can be expected to have an activation energy lying between 5 and 10 kcal. Normal C—H bond energies plus the known heat of dissociation of $H_2$ would say that the reaction is about 5.5 kcal exothermic; thus the $E_{act}$ should be low, as suggested. However, the best current figure for the bond-dissociation energy of the first C—H bond in acetylene is 114 kcal. Hence the reaction is in fact about 11 kcal endothermic, and the activation energy should be of the order of 17 kcal, in the forward direction, by virtue of the fact that one now computes the activation energy of the back reaction to be about 6 kcal [by the Hirschfelder Rule (*18*)].

It is not the purpose of the present note to criticize particularly the use of incorrect heats of atomization in the compilation of tables of bond energies by different authors. Nevertheless, it seems appropriate to add a note of caution to the effect that one should not mix bond energies in calculations if they are drawn from different sources unless one is absolutely sure that they are based upon the same heat of sublimation of carbon and the same heats of dissociation of $N_2$ and $F_2$ (and, incidentally, the same reference temperature and the same averaging procedures). The 298°K values of these now accepted are, respectively, 170.9 kcal, 225.1 kcal, and 37 kcal.

To conclude, let us return briefly to the matter of nomenclature, and try to sum up our views. The noun "strength" is felt to be of qualitative use, but it should be avoided in quantitative contexts. "Bond energy," "mean bond energy," "average bond energy," and "bond energy term" may all be taken to mean the same thing, with the qualification that the basis for computation should always be indicated by authors and examined by readers. "Bond energy" should never be used to mean "bond-dissociation energy"; nor should phrases such as "the energy necessary to break the bond" or "heat of dissociation of a bond" ever be used when what is meant is actually the bond energy. "Normal covalent single-bond energy" is a quantity that generally differs from the bond energy of single bonds except in the case of homonuclear, single-bonded diatomics. It is of great interest in the theory of chemical bonding (*4*). Finally, "resonance energy" is not synonymous with any of the other terms discussed here, but is related to bond energies as an empirical quantity. It arises in cases where a molecule may not be assigned a unique valence structure, and represents the difference between the experimental heat of atomization of the molecule and that computed using bond energies and an arbitrarily assumed structure. The classical example of its use in discussing molecular structure (*4*) is the benzene molecule. It is also of importance in making approximate calculations of heats of reaction, and for this purpose it is particularly useful to have tabulations of empirical resonance energies in representative organic molecules, to which analogies may be drawn in considering new substances whose heats of formation are not known (*11*).

The more that information on bond-dissociation energies becomes available, the less need there is to use bond energies in rough calculations. However, all indications point to a lengthy continuation of the present state of affairs, viz., a greater rate of synthesis or discovery of new chemical species than of the determination of new bond-dissociation energies in molecules and radicals. Thus bond energies will continue to be important in pure and applied physical and organic chemistry. We hope that the comments herein may, directly or indirectly, ease the struggle for understanding on the part of at least some students of these topics.

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# Inexpensive Stuart-type Molecular Models

The great usefulness of molecular models as a teaching aid and guide to research workers has prompted the design of many types of models.[1] One of the most popular types was originated by Stuart[2]; these models depict both the covalent and the Van der Waals radii. Although excellent Stuart model sets are available commercially[3] such sets usually contain only a fraction of the kinds of atoms necessary to depict many interesting inorganic systems. The synthetic ingenuity of modern organic and inorganic chemists continually widens this gap. To meet the need for a wider variety of atoms at reasonable cost (of the order of a few cents per atom) we have developed a procedure for the inexpensive duplication, in plastic, of original atomic prototypes. Prototypes of new atoms may be made from wood and duplicated in plastic (Fig. 1).

The general design of a Stuart-type model involves a sphere proportional to the Van der Waals radius of the atom. Faces are cut on the sphere, at proper angles, corresponding to the covalent radii.[2,4] Inspection of the data on interatomic distances shows that covalent radii of constituent atoms are not always strictly additive.[4] Van der Waals radii are also variable. Thus, while the Van der Waals radii of most atoms are very close to their ionic radii, we find in the case of hydrogen an ionic radius of about 1.5 Å and a van der Waals radius of 1.2 Å in hydrocarbons.[5,4] In glycine the apparent radius of hydrogen varies from 1.06 to 1.34 Å.[4] If steric interactions are of interest it is clearly necessary to have several sizes of hydrogen available.

From the standpoint of convenience and versatility, pegs are the best devices for connecting atomic models. The use of pegs permits some variation in bond length when appropriate washers are inserted between atoms. Short lengths of polyethylene tubing serve well as connecting pegs. When about 0.25 in. o.d. tubing is used and the models are made to the scale 1 cm = 1 Å the models are compatible with Catalin models.[3a] It is thus possible to supplement standard Catalin sets.

Materials necessary for the construction of these models are relatively inexpensive. Liquid rubber (latex), which is needed for the molds, is available at most hobby shops (a quart, sufficient for roughly 100 molds, costs about $4). Silicone rubber lacks the strength necessary for molds which are to be used repeatedly. Resins (either polyester or epoxy) can be obtained from boat shops as well as the sources listed below.[6] Epoxy resin costs about $15 per gallon, a quantity sufficient for approximately 500 atoms; polyester resin costs about $6 per gallon. Although both types of resin are satisfactory for model making we found polyester superior in handling properties as well as in price.

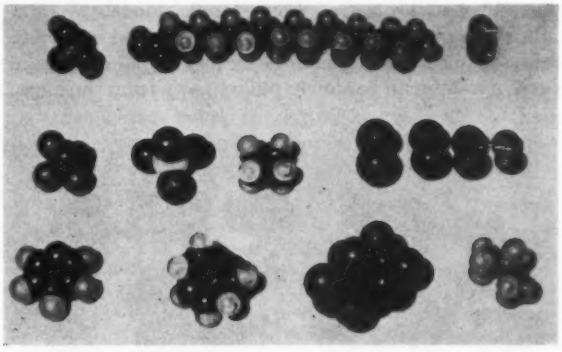

**Figure 1. A collection of molecular models which have been produced by the procedure described in the text. From left to right, top row: sulfuric acid, stearic acid, carbon dioxide; second row: phosphorus pentafluoride, gallium tetrachloride anion, cyclobutane, the halogens; bottom row: pyridine, cyclooctatetraene, *n*-perchlorobutane, the $H_2B(NH_2)_2^+$ cation.**

Resin may be colored with mineral pigments (available at paint stores), or oil-soluble, *p*H insensitive pharmaceutical dyes, etc. This method of coloring is superior to painting after casting, both in time consumed and in finished appearance. Polyethylene tubing is available from scientific supply houses (about 15¢ per foot).

### Model Making Procedure

Before making molds, all holes in selected prototypes must be filled with modeling clay to leave flat faces which will release easily from the molds. Holes for bonds may be drilled in the models after casting. The molds are best poured on a sheet of glass. This permits examination of the undersurface for undesirable bubbles (which may be destroyed by a pinprick while the rubber

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[4] Pauling, L., "Nature of the Chemical Bond," 3rd. ed., Cornell Univ. Press, **1960**, Chap. 7.

[5] Hurd, D. T., "Chemistry of the Hydrides," John Wiley & Sons, Inc., **1952**, pp. 17, 25.

[6] (*a*) Defender Textile Corp., 380 Broadway, New York 13, N. Y.; (*b*) Adhesives Dept., Raybestos-Manhattan Inc., Bridgeport, Conn.

is still fluid) and observation of the color change taking place as the latex cures. After curing, the molds release easily from the smooth surface of the glass.

A small amount of liquid latex is brushed onto the glass, and the prototypes are placed on this rubber so that a thin coat (roughly 0.3 mm) will be beneath each prototype. This step is essential in order to obtain molds with well-formed faces. After all of the protypes have been placed on the sheet, liquid latex is brushed onto each to produce a coating roughly 0.5 mm thick. An even coating free from bubbles is desirable. For convenience in handling and storage it is suggested that several molds be connected together to form a sheet (Fig. 2). Such a sheet helps keep molds level while they are being filled with plastic. The cured molds may be identified by writing the relevant chemical symbols directly on the rubber with a ball point pen. Ordinarily about 24 hours should pass before applying a second coat. The number of coats required will depend chiefly on the model size. The larger the prototypes, the thicker must be the mold in order to insure its rigidity when filled with plastic. For example, models of 1 cm radius require only two coats, while those of 2 cm radius require four. When the rubber is well cured, the sheet of molds can be slowly pulled away from the glass.

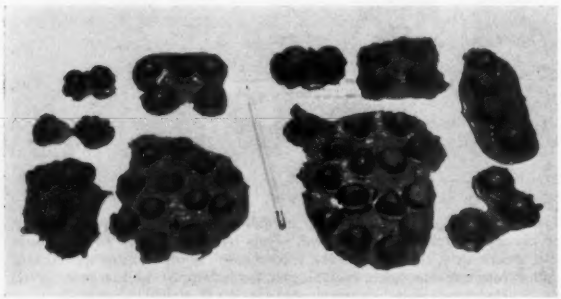

Figure 2. The underside of some rubber molds.

Each prototype is then removed with the help of a razor blade, by carefully cutting away the thin rubber film that covers its face. Care must be taken to prevent this film (which may be tacky because of lack of contact with the air) from sticking to the interior of the mold. When all of the face coverings have been removed, the prototypes are carefully popped out through the relatively small opening. The molds are now ready for filling (Fig. 3).

If epoxy resin is used, such as that available from Raybestos-Manhattan, it is desirable to coat the inside of the mold with a small amount of Dow-Corning silicon stopcock grease. If a polyester resin is used such as that available from Defender Textile Co., no release agent is necessary.

The base and catalyst are mixed together in proportions suggested by the manufacturer, together with any desired coloring matter or filler. Epoxy resin is usually quite viscous and occludes bubbles on mixing; it is therefore desirable, in order to produce attractive models, to expose the resin to a vacuum before pouring. An ordinary vacuum desiccator attached to a water aspirator is convenient for this purpose. A small amount of acetone poured onto the surface of the plastic before exposing to vacuum aids in breaking the bubbles that form on the surface. A container two or three times the volume of the plastic is usually large enough to prevent overflow of the foam produced upon evacuation. It is frequently necessary to apply and release the vacuum several times to remove the bubbles. Using polyester resin there is no difficulty with bubble formation; the material flows freely and bubbles coming to the top may be pierced with a pin.

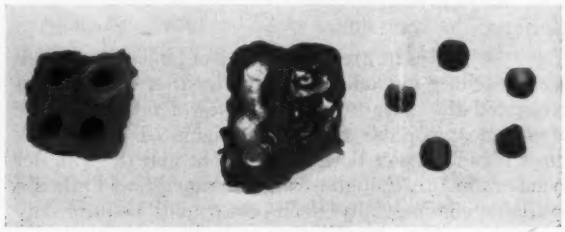

Figure 3. An empty mold, a filled mold, and a collection of boron atoms immediately after removal from a mold.

The molds are then filled with resin. Epoxy resin does not shrink on setting, so filling just to the top is sufficient. The molds may be squeezed gently from below to dislodge air bubbles forming at the surface of the molds. In contrast to epoxy resin, polyester shrinks noticeably so that an excess of plastic is needed at the top of the mold. Setting may be accelerated by placing the molds in a 50°C oven (a 100° oven damages the molds); acceleration is particularly desirable with epoxy models, which may take several days to set up. Polyester models will set in one hour, with the proper amount of catalyst. Larger amounts of catalyst shorten the setting time, but may produce enough heat to damage the molds or crack the models.

Beakers and other materials which have been used in the model-making process may be cleaned with acetone before the resin has set. Because of the long time interval before the epoxy resin sets up, it is practical to catalyze a large batch for storage at low temperature. We have been able to use epoxy which had been kept for over a month at the dry ice temperature.

After sufficient models have been cast and removed from the molds, the rough faces from the open sides of the molds are ground flush with sandpaper (a sanding disk in a table saw is convenient). Next, holes are drilled in the faces for bonds. Holes of $^{15}/_{64}$ in. diameter, about $^{6}/_{10}$ cm deep, are satisfactory. Pieces of polyethylene tubing, about $^{1}/_{2}$ in. o.d., $^{1}/_{8}$ in. i.d., and 1 cm in length, are a snug fit in such holes.

To drill the holes, the models may be clamped on a drill press stand or placed in a wooden jig. A simpler procedure, if the equipment is available, is to drill the models on a lathe. For this process most models can be held with a three jaw chuck, which makes centering of the holes particularly easy.

The drilled models may be slightly countersunk manually with a large ($^{1}/_{2}$ in.) drill to facilitate insertion of the bonds. If coloring matter was not added to the resin the models may then be painted.

The interest and material assistance of Dr. R. W. Parry and Mr. Oliver D. Steiner are gratefully acknowledged.

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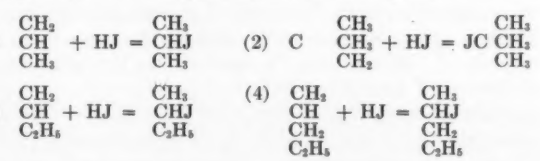
# The Markovnikov Rule

The Markovnikov Rule is one of the best-known of the empirical rules of organic chemistry. It is encountered at an early stage in the teaching of organic chemistry; it is comprehensive and easy to remember and it is capable of clear theoretical explanation even at an elementary level. Yet it is often stated in a form appreciably different from that in which it was enunciated by Markovnikov, and it was the subject of an interesting controversy between Markovnikov and L. Henry.

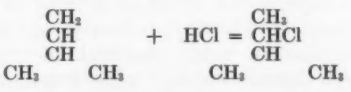
The first statement of the Rule in an accessible journal seems to have been in Liebig's *Annalen* in 1870 (*1*) under the somewhat uninformative title "Communications from the Chemical Laboratories at Kazan" [where Markovnikov was at that time a professor (*2*)]. A large section of the communication was devoted to a study of the isomeric hydroxybutyric acids; the intermediate for the synthesis of one of the isomers was propylene chlorhydrin, derived from propylene by direct addition of hypochlorous acid. After some discussion of the apparently contradictory modes of addition of hypochlorous acid to propylene and to "butylene" (by which Markovnikov meant *iso* butylene from the formula given) Markovnikov decided that it was not possible to propose a general rule for the addition of "(OH)Cl" to unsaturated hydrocarbons. He went on to say that such a rule could be formulated for the addition of hydrogen halides to unsaturated compounds; then followed the original statement of the Markovnikov Rule:

> When a hydrocarbon of unsymmetrical structure combines with a halogen hydracid the halogen adds itself to the less hydrogenated carbon atom, i.e. to the carbon which is more under the influence of other carbon (atoms).

As examples of the Rule relating to hydrocarbons Markovnikov quoted the addition of hydriodic acid to propylene, to two butylenes, and to an amylene:



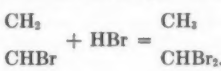
and of hydrogen chloride to another amylene



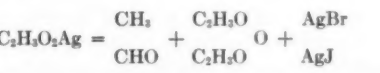
Markovnikov then extended the Rule to include unsaturated compounds having a halogen atom already attached to one of the carbon atoms forming the double bond:

> In the addition of hydrochloric, hydrobromic, or hydriodic acids to vinyl chloride, chlorinated propylene and other analogues, the halogen adds to the carbon atom which is already bound to a halogen (atom).

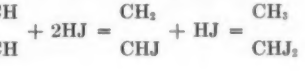
The examples quoted for this extension of the Rule are interesting because less obvious (apart from the addition of hydrobromic acid to vinyl bromide to give ethylidene bromide and not ethylene dibromide:



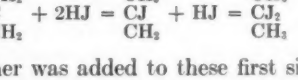
Thus, Pfaundler had reported (*3*) that the product of addition of hydriodic acid to vinyl bromide gave, on treatment with silver oxide and acetic acid, aldehyde (acetaldehyde). Markovnikov interpreted this reaction as follows:



Using more highly unsaturated compounds as examples Markovnikov noted that acetylene adds on two molecules of hydriodic acid (a process used in its purification) to give "an isomer of ethylene iodide."



and allylene



Nothing further was added to these first simple statements of the Markovnikov Rule until 1874, when L. Henry, already well-known for his work on allylic compounds, published a paper "On the products of addition of propylene to hypochlorous acid" (*4*). This paper commenced with a statement of a general law bearing a considerable resemblance to Markovnikov's Rule, but with no mention of Markovnikov in this connection. The general law was

> When a molecular system XX′, made up of simple or compound radicals, different in nature, quality, and chemical energy approaches an unsaturated compound $C^nH^m$, . . . , Y containing unsaturated carbon atoms unequally hydrogenated, such as $CH^2$, CH, and C, the radical X, negative or more negative, attaches itself to the least hydrogenated carbon atom, and the radical X′, less negative, the 'positive' radical either absolutely or by comparison, attaches itself to the more hydrogenated carbon atom.

This was a much more general law than that stated by Markovnikov, and Henry went on to say that the law was confirmed, notably, by the mode of addition of hypochlorous acid; that there were numerous examples to prove this, but that he would deal only with the

allylic derivatives. He had previously reported that allylic derivatives $(C^3H^5)X$ combine readily with a molecule of (OH)Cl to give glycerol chlorhydrins which are primary alcohols; hence they must be

$$\begin{matrix} CH^2X \\ CHCl \\ CH^2OH \end{matrix}$$

Since allyl derivatives are merely primary derivatives of propylene, then propylene should add on (OH)Cl to give

$$\begin{matrix} CH^2OH \\ CHCl \\ CH^3 \end{matrix}$$

But Markovnikov in his paper had stated that the chlorhydrin of propylene was a secondary alcohol, since on oxidation with dichromate and sulfuric acid it gave chloro-acetone. This, in Henry's opinion, constituted the sole exception to his law and he wrote

> In spite of all the esteem in which I hold the fine works of M. Markovnikov, and the authority of his name, I cannot, after reflection, accept his opinion as the truth. I have re-read his work attentively; it is irreproachable as regards the facts, and I admit the reality of all the experimental details contained in it; but I reject the conclusion as to the nature of the addition product from propylene and hypochlorous acid. This conclusion is not justified, in a rigorous or certain manner, by any fact.

Henry pointed out subsequently that the structure of this product of addition could be proved either by reduction or by oxidation. On reduction one possible chlorhydrin would give normal propanol, and the other iso-propanol; on oxidation one would give chloro-acetone (as Markovnikov had already reported) and the other chloropropionaldehyde. He also pointed out that the properties reported by Markovnikov for his 'chloro-acetone' were those to be expected for chloropropionaldehyde. Finally Henry announced that he had oxidized propylene chlorhydrin beyond the point reached by M. Markovnikov and that he would publish the results in a subsequent communication.

Before this other evidence was forthcoming, however, Markovnikov had replied with three communications under the title "On the laws which govern direct addition reactions" which were submitted by Wurtz and published in *Comptes rendus* (*5*, *6*, *7*). In the first of these Markovnikov's Rule was presented in its final and more general form, obviously much modified by Henry's intervention. Markovnikov commenced his paper with a re-statement of the Rule in its original form, "in which state the question has remained for more than five years," and noted that "among the studies concerning these laws were those of M. Henry." Further "that in studying derivatives of the allyl group this chemist has arrived at conclusions, of which the resemblance to those that I have advanced seems to have escaped his attention." He then discussed Henry's view of direct addition and decided that both Henry's law and his own Rule were too "absolute," and required qualification ("It seems to me that the form given by M. Henry is too absolute and does not always coincide with the views of other chemists"). The direction of addition is obviously dependent on the conditions of the reaction, of which Markovnikov mentions temperature. Reboul had shown that monobromopropylene added hydrobromic acid to give either $CH^3CHBrCH^2Br$ or $CH^3CBr^2CH^3$ depending on the conditions used.* Markovnikov then proposed the final form of his Rule:

> When a molecular system YZ approaches an unsaturated molecule $C^nH^mX$ at low temperature, the more negative element or group Y combines with the less hydrogenated carbon atom, or with that which is directly attached to some negative element; but at comparatively higher temperatures, it is the element Z which combines with the less hydrogenated carbon (atom), that is to say that, for the same substances, the reaction takes a direction exactly opposite from the first.

In his next paper, Markovnikov noted that the uniformity of addition is often masked, since ordinarily both possible products of addition occur together. The proportions of the isomers formed varies according to the conditions of reaction, and this led Markovnikov to the conclusion that it should be possible to control the direction of addition.

On the structure of propylene chlorhydrin, Markovnikov's reasoning was less assured. He pointed out that Butlerov had reduced the chlorhydrin to 'pseudo-propyl alcohol,' but then went on to discuss the formation of the dichlorhydrin of glycerol from epi-chlorhydrin

$$\begin{matrix} CH^2Cl \\ CH \\ \quad O \\ CH^2 \end{matrix} + HCl \rightarrow \begin{matrix} CH^2Cl \\ CHOH \\ \\ CH^2Cl \end{matrix}$$

He concluded that attachment of the hydroxyl group to the less hydrogenated carbon atom during this reaction indicated that the hydroxyl group had a greater affinity for such a carbon atom—a *non sequitur* that Henry was quick to point out in a subsequent paper. But Markovnikov ended his paper by stating once more that there were two contradictory findings for the addition of hypochlorous acid to unsaturated hydrocarbons and hence no definite rule could be advanced for this addition. In his final paper (*7*) on this subject, Markovnikov gave experimental details of his oxidation of propylene chlorhydrin and his isolation of monochloro-acetone, pointing out that chloro-acetaldehyde is readily oxidized (in the air) and hence that chloropropionaldehyde was unlikely to be isolated from an oxidation mixture.

This seems to have been Markovnikov's last word on his Rule, or on the oxidation of propylene chlorhydrin, but Henry produced two further papers (*8*, *9*) also in 1876, on the oxidation experiments. Henry began (*8*) by stating that he had attempted to establish the *law of addition of hypochlorous acid*, and at the same time to oppose M. Markovnikov's opinion on the particular structure of propylene chlorhydrin (Henry's law, reproduced above, was in fact quite general, and was *not* referred to as a law of addition of hypochlorous acid.) Henry also protested that Markovnikov had used a different oxidizing agent (dichromate and sulfuric acid) and that in experiments using nitric acid as oxidizing agent the major product from propylene chlorhydrin was chloropropionic acid, identical in "properties, analysis, and vapour density" with a sample derived from lactic acid. Furthermore, since Henry's oxidation product was chloropropionic acid, Markovnikov's

* An early example of the confusion that was to grow until the work of Kharasch in the 1930's.

must be chloropropionaldehyde. Henry then enunciated his law of addition of hypochlorous acid:

> In the addition of hypochlorous acid OH,Cl to an unsaturated compound containing the system CH=CH², the hydroxyl attaches itself to the more hydrogenated carbon, and the chlorine to the less hydrogenated carbon.

He pointed out that there was no evidence to justify the extension of this law to the systems —C≡C—, C≡CH, or CH≡CH, but that he proposed to fill in this gap in knowledge. He then advanced two reasons why the chlorine should be considered as the more electronegative part of (OH)Cl:

> First, chlorine is more electronegative than oxygen; as for hydrogen it constitutes a positive element, following the happy expression of M. Dumas, a gaseous metal, therefore the O, associated with an atom of hydrogen (OH) must be less negative than chlorine.
>
> Second, the hydroxy HO in the form HO—OH, easily expels iodine from alkaline earth iodides, but not the Cl of corresponding chlorides.

Henry added a coda with two main points—first, that he had considered only addition of hypochlorous acid to hydrocarbons (excluding cases where the unsaturated carbon atom bore a negative substituent); and second, that he had ignored the effect of temperature since all the experiments made with hypochlorous acid were in fact made in the cold.

> Finally, I do not hesitate to recognize that Mr. Markovnikov was the first to formulate a general law pertaining to the products of addition to unsaturated bodies. If I have not mentioned this, it was that I could not go into the history of the question in a Note, and that it seemed superfluous to mention facts known to all chemists. Having taken the part of my *savant contradicteur*, perhaps he will permit me to claim for myself the law of addition of HOCl.

On this fairly amicable note the direct controversy between Henry and Markovnikov would appear to have ended. Markovnikov's experimental results were confirmed in 1895, by Michael (*10*), who isolated chloroacetone (as its semicarbazone) from the oxidation products of propylene chlorhydrin; Michael also showed that Henry's "chloropropionic acid" was very largely chloro-acetic acid. Subsequently Krassousky (*11*) re-examined the addition of hypochlorous acid to isobutylene (an addition which was thought by Markovnikov to be anomalous) and showed that in this case also the hydroxyl group becomes attached to the less hydrogenated carbon atom, giving a secondary alcohol. Finally, in 1902, Tiffeneau (*12*) published further evidence for 'Markovnikov addition' of hypochlorous acid to unsaturated hydrocarbons, but was unwise enough to begin his article:

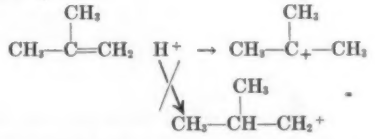
> In 1875, Markovnikov had shown, *contrary to the assertions of Henry*, that in the addition of ClOH to propylene, the hydroxyl is attached to the less hydrogenated carbon atom giving the chlorhydrin $CH^3CHOHCH^3Cl$.

Within a month a reply from Henry (*13*) appeared, taking exception to this remark, and re-iterating his former arguments. Henry appeared to be in ignorance of Michael's paper, as he still maintained that the oxidation product was chloropropionic acid, although admitting that Markovnikov had isolated chloro-acetone. Henry ended by saying that he intended to re-examine the problem; the results of his re-examination were embodied in two last papers on this addition. In the first (*14*) he reported unambiguous syntheses of the two possible propylene chlorhydrins (called $\alpha$- and $\beta$-) and an examination of their behaviour with the oxidizing agents nitric acid and acid dichromate:

$$\underset{\alpha}{CH_3CHOHCH_2Cl} \qquad \underset{\beta}{CH_3CHClCH_2OH}$$

Nitric acid on the '$\alpha$-chlorhydrin' gave first chloronitrosoacetone, and then a mixture of acetic and chloroacetic acids. Dichromate mixture with the $\alpha$-chlorhydrin gave a poor yield of mono-chloroacetone. Oxidation of the $\beta$-chlorhydrin gave a poor yield of $\alpha$-chloropropionic acid, with no chloroacetaldehyde, but "it is not surprising that chloropropionaldehyde is not formed in the oxidation, as I have shown by direct experience that $\alpha$-chloropropionic acid itself is oxidized to acetic acid under these conditions." Henry's final words on the subject were contained in a lengthy summary of the controversy (*15*) wherein he concluded that the product of addition of hypochlorous acid to propylene was a *mixture* of the two possible chlorhydrins with Markovnikov's candidate ($\alpha$ above) in the major proportion. However, he remained convinced that hypochlorous acid added to isobutene in the opposite sense, and he made a number of somewhat slighting remarks about "un chimiste americain M. Arthur Michael" who held the opposing viewpoint.

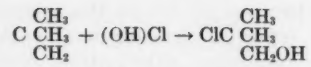
It is interesting to compare the current interpretation of electrophilic addition with Markovnikov's ideas. Thus, in the addition of HX to an ethylenic double bond, the proton adds on to give an intermediate carbonium ion. It is supposed that the double bond is polarized on approach of the proton in a sense which is determined by hyperconjugation with alkyl groups attached directly to the ethylenic carbon atoms; it should also be noted that the more stable carbonium ion will be that which carries the largest number of alkyl groups around the positively charged carbon atom; thus



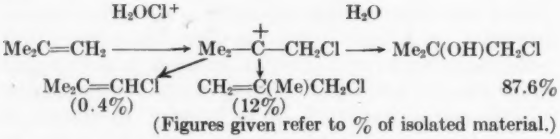
Markovnikov's original Rule contained a statement that the halogen atom in HX will go to that "most influenced by surrounding carbon atoms" which is in close accord with current theory. It is also currently accepted that at higher temperatures the homolytic fission of the reagent becomes important with a concomitant change in mechanism, and hence in position of attachment of the halogen atom:

$$CH_3CH{=}CH_2 + Br\bullet \rightarrow CH_3{-}\dot{C}H{-}CH_2Br$$
$$CH_3\dot{C}HCH_2Br + HBr \rightarrow CH_3CH_2CH_2Br + Br\bullet, \text{ etc.}$$

The addition of hypochlorous acid is more interesting since Henry's views appear more logical and yet Markovnikov's were correct. The fallacy in Henry's arguments lay in his assumption that hypochlorous acid is (HO)Cl, and was encouraged by the confusion in the literature—for example, by Butlerov's report that the addition of hypochlorous acid to isobutylene proceeded thus:



This addition has been studied by de la Mare (*16*) who reported that the product was mainly 1-chloro-2-methylpropan-2-ol, confirming the generally accepted view that the initial addition is of the hypochlorous acidium ion $H_2OCl^+$ (or $Cl^+$ if hydrogen chloride is present) to give the carbonium ion shown below; the second stage is addition of the nucleophilic solvent (water). The only isolated by-products were ethylenic arising by elimination of a proton from the carbonium ion:



(Figures given refer to % of isolated material.)

It is known (*17*) that none of the anti-Markovnikov addition product (2-chloro-2-methyl propan-1-ol) is formed in the reaction.

In Markovnikov's Rule, therefore, we have an excellent pedagogic example of the way in which an empirical generalization can be subsequently correlated with a general theory, while at the same time illustrating the experimental difficulties which made correct generalizations remarkable in the early days of organic chemistry.

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*Textbook Errors, 31*

# The Pyrolytic Decomposition of Carboxylate Salts to Ketones


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A number of organic chemistry textbooks[1] state that acetone is obtained when dry barium or calcium salts of acetic acid are heated. These texts usually extrapolate this statement to include the pyrolytic decomposition of all calcium or barium carboxylates to carbonyl compounds.

However, critical examination of the chemical literature discloses that such statements are not warranted with respect to the salts, although excellent yields of ketones can be obtained by the vapor phase decarboxylation of the carboxylic acids themselves over a variety of catalysts (*1*). The topic has four aspects: pyrolytic decomposition of carboxylate salts to simple ketones, of mixed carboxylate salts to mixed ketones, of dicarboxylate salts to cyclic ketones, and of mixed carboxylate and formate salts to aldehydes.

Most of the chemical literature on this topic is very old; the earliest statements repeatedly confirm the observation that dry distillation of calcium acetate does indeed yield acetone; technical manuals in use up to 1914 describe the preparation of acetone from "grey acetate of lime" (the calcium salt of pyroligneous acid).

With the exception of the transformation of calcium phenylacetate into dibenzyl ketone in 83% yield (*2*), there is virtually no literature devoted to a scrupulous study of composition and yield of reaction products obtained from the dry distillation of calcium or barium carboxylates. The mere observation that hosts of investigators have attempted (with considerable success in some instances) to prepare ketones from other than barium and calcium carboxylate salts provokes a

Suggestions of material suitable for this column and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, Calif.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not to evaluate individual texts, the source of errors discussed will not be cited. To be presented, the error must occur in at least two independent standard books.

suspicion of dissatisfaction on the part of many investigators with the products obtained by pyrolysis of barium and calcium carboxylates.

Fittig (*3*) reported that the dry distillation of calcium acetate gave a neutral product, with a boiling range of 60–130°, from which he isolated acetone, methyl ethyl ketone, $C_5H_{10}O$, and $C_6H_{10}O$; no yields were reported.

Limpricht (*4*) stated that calcium *n*-butyrate gave a liquid product with a boiling range of 144–222°. From this were isolated eight compounds, aldehydes as well as ketones. Two ketones, $C_8H_{16}O$ and $C_{10}H_{20}O$, were isolated and analyzed, but not characterized.

Friedel (*5*) also studied the products obtained from the pyrolysis of calcium *n*-butyrate; he isolated from the reaction mixture *n*-butyraldehyde, methyl *n*-propyl ketone, ethyl *n*-propyl ketone, and di-*n*-propyl ketone; however, he did not report the presence of $C_8H_{16}O$ or $C_{10}H_{20}O$ ketones.

Barbaglia and Gucci (*6*) distilled 2 kg of dry calcium isobutyrate; 580 g of ketone mixture boiling at 55–165° was obtained. Diethyl ketone, methyl isopropyl ketone, ethyl isopropyl ketone, diisopropyl ketone, isobutyraldehyde, and even pinacolone were obtained from the reaction mixture!

Nef (*7*) attempted to rationalize these results by postulating loss and gain of methylene radicals from the organic moieties present in the salts.

Two references (*8*, *9*) are cited for the preparation of mixed ketones from the pyrolytic decomposition of mixed salts of barium acetate with higher molecular weight barium carboxylates; 60% yields were claimed by Morgan and Holmes (*9*). However, no mixed ketones other than methyl ketones are reported to have been prepared by this method.

Frequently this reaction is also cited as a method for the preparation of cyclic ketones from salts of dicarboxylic acids. Yet Kon (*10*) pyrolyzed calcium β,β-dimethylglutarate to give a distillate with a boiling range of 100–280°! From this distillate were isolated 30% acetone, 5% mesityl oxide, 33% isophorone, and unstated amounts of unsaturated hydrocarbons.

Zelinsky (*11*) distilled calcium sebacate to yield a "cyclononanone" with the following properties: bp 95–97° (17–18 mm), $d_4^{22.5}$ 0.8665, $\eta_D^{22.5}$1.4412, semicarbazone mp about 105°, oxidized to an acid of mp 99°. Several years later the incomparable work of Ruzicka and Brugger (*12*) cited the unequivocal synthesis of cyclononanone (in low yields, however, by distillation of thorium sebacate) with markedly different properties: bp 93–95° (12 mm), $d_4^{17}$0.9587, $\eta_D^{17}$1.4730, semicarbazone mp 178–179°, oxidized to azelaic acid of mp 106°. In addition, Ruzicka and Brugger reported that other cyclic ketones and methyl *n*-octyl ketone were isolated from their reaction mixture.

Several organic chemistry texts and laboratory manuals report the preparation of cyclopentanone in good yield by distilling adipic acid from small amounts of calcium or barium oxide. But private communications, corroborated by laboratory observation by the authors, indicate that mere slow distillation of pure adipic acid gives excellent yields of cyclopentanone! Large chemical manufacturers are plagued by this undesired intramolecular decarboxylative cyclization of adipic acid.

The statement that aldehydes are obtained by pyrolytic decomposition of mixed salts of calcium formate and higher calcium carboxylates seems to be based upon one report over a century old, that of Piria (*13*). No quantitative results were cited by this investigator.

For the most part none of these references support the sweeping generalizations made in many texts of organic chemistry concerning the utility of the pyrolytic decompositions of calcium or barium carboxylates into simple ketones, mixed ketones, cyclic ketones, or aldehydes.

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# A Group Experiment on the Hammett Sigma-Rho Relation

The second-order hydrolysis of an ester by aqueous alkali (*1*) is a familiar kinetic experiment in laboratory courses of physical chemistry. The present article discusses a broadening of this exercise so as to introduce the problem of relating chemical reactivity to structure, and in particular the Hammett $\sigma\rho$ relation. The only important changes in the usual procedure are that each student determines the rate constant for a different ester, and the combined results are then considered by the class. This adds a little to the trouble of supervision. On the other hand the vigorous development in recent years of the Hammett relation and its offshoots (known collectively as "linear free energy relations") probably deserves greater recognition in teaching courses, and the writer believes this practical approach to be particularly suited to the subject.

## The Hammett Relation

The rate-determining step in the alkaline hydrolysis of methyl benzoate is considered to be attack on the carbomethoxy group by hydroxide ion (*2*). As expected from simple electrostatic considerations, meta and para substituents which are electron-attracting relative to hydrogen accelerate the hydrolysis, while electron-donating substituents retard it. (Similar predictions for ortho substituents are vitiated by steric interactions). It was shown by L. P. Hammett (*3*) that each meta and para substituent can be assigned a numerical value (the *substituent constant*, $\sigma$) which quantitatively governs its effect upon the rate of this and many other side-chain reactions of benzene derivatives. As can be seen from Table 1, which gives substituent constants relevant to this exercise, electron-attracting substituents have positive values and electron-donating substituents have negative values.

**Table 1. Hammett Substituent Constants (*4*)**

| Substituent | $\sigma$ | Substituent | $\sigma$ | Substituent | $\sigma$ |
|---|---|---|---|---|---|
| $p$-$C(CH_3)_3$ | −0.197 | $p$-$C_6H_5$ | 0.009 | $p$-Br | 0.232 |
| $p$-$CH_3$ | −0.170 | $p$-F | 0.062 | $p$-I | 0.276 |
| $m$-$C(CH_3)_3$ | −0.120 | $m$-$OCH_3$ | 0.115 | $m$-F | 0.337 |
| $m$-$CH_3$ | −0.069 | $p$-CHO | 0.216 | $m$-CHO | 0.355 |
| None | 0.000 | $m$-$C_6H_5$ | 0.218 | $m$-Cl | 0.373 |
| | | $p$-Cl | 0.227 | $m$-Br | 0.391 |

If the logarithms of rate constants for the alkaline hydrolysis of methyl benzoates in aqueous acetone at 15°C are plotted against corresponding values of $\sigma$ the points fall about a straight line of slope 2.30. For $\sigma = 0$ the appropriate rate constant is the one for methyl benzoate itself, $k_0$. Hence

$$\log k/k_0 = 2.30\,\sigma$$

This is the Hammett relation for the particular reaction considered. The same form holds for other side-chain reactions but the numerical coefficient varies with the reaction: E.g., it is 1.07 for the alkaline hydrolysis of meta and para substituted benzamides in water at 100°C, and −2.14 for the quaternization of dimethylanilines by methyl iodide in methanol at 65°C, a reaction which differs from the previous two in that electron-attracting substituents retard the rate. This coefficient (the slope of the line obtained by plotting $\log k$ versus $\sigma$) is called the *reaction constant*, $\rho$, and the general form of the Hammett relation is therefore

$$\log k/k_0 = \sigma\rho$$

For each reaction series several rate constants must be measured in order to determine $\rho$. Other rate constants in the series can then be calculated, including those of compounds having more than one substituent, for which cases the sum of the substituent constants is used in place of $\sigma$. The Hammett relation applies as well to equilibrium constants as to rate constants, and the scales of $\sigma$ and $\rho$ are actually based on an equilibrium series, the ionization of benzoic acids in water at 25°C. The reaction constant is arbitrarily taken as unity for this series, and the values of $\sigma$ are calculated from the identity

$$\sigma \equiv \log K/K_0$$

The Hammett relation is approximate. (The rate or equilibrium constants are predicted with an average deviation of about 15%.) It is essentially empirical, for although it can be rationalized it cannot be derived from fundamental physical laws (*5*). In spite of these disadvantages it is of great value. Firstly, the values of $\sigma$ and $\rho$ listed in 1953 [in an important review by H. H. Jaffé (*6*)] enable 42,000 rate and equilibrium constants to be calculated; the majority of these have not been measured, and many are experimentally inaccessible. Secondly, $\rho$ describes quantitatively the susceptibility of these reactions to polar effects within the molecule, and it is for this reason a valuable criterion of mechanism (*7*). (The information required for both these purposes can be very succinctly expressed. It is usual to record the "least squares" values of $\rho$ and $\log k_0$, the number of measurements ($n$) on which these are based, and suitable statistical estimates of the scatter, so that the reliability of the data can be assessed.) Finally, the success of the Hammett relation has led to the discovery of similar relations in other systems, and to other developments in the field of chemical reactivity (*8*). [For an explanation of the term "linear free energy relation," which is applied to all relations of the Hammett form, see reference (*9*).]

## The Experiment

Alkaline ester hydrolysis is among the most convenient of hundreds of reactions which might be used to illustrate the Hammett relation: many suitable esters are commercially available, others are easily prepared from the corresponding acids, and the reactions can all be followed by a simple titrimetric method. The following instructions (*10*) apply to the hydrolysis in 56% acetone-water at 15°C of methyl benzoate itself. Necessary modifications when dealing with other esters and the choice of alternative working temperatures are considered later.

*56% (by weight) acetone-water.* Transfer 200 ml of water to a 500-ml volumetric flask and fill to the mark with acetone. Use distilled water through which air has been bubbled to ensure that $CO_2$ is not in excess of the equilibrium concentration.

*0.2 N sodium hydroxide in 56% acetone-water.* Transfer 50 ml of approximately 1 *N* aqueous $CO_2$-free sodium hydroxide and 79 ml of acetone to a volumetric flask, and make up to 250 ml with 56% acetone-water. Standardize with pure benzoic acid, using Cresol Red indicator.

*Hydrochloric acid.* Prepare about 700 ml of 0.015–0.020 *M* aqueous hydrochloric acid. The equivalent volumes of this and the sodium hydroxide solution are then determined under the conditions of the reaction, so as to find the titration value for time $t = 0$. Pipet 50 ml of the alkali and 50 ml of 56% acetone-water into a flask and immerse in a constant temperature bath at 15°C for 15 minutes. Titrate 10-ml samples with the acid, using Cresol Red.

*The ester solution.* Prepare 250 ml of a solution of methyl benzoate in 56% acetone-water such that the concentration is exactly half that of the sodium hydroxide solution.

*First kinetic run.* Pipet 50 ml of the sodium hydroxide into one compartment of the reaction vessel, and 50 ml of the ester solution into the other. (A suitable reaction flask is made by heating the base of a 500-ml conical flask along a diameter and pushing inward with the edge of an asbestos board.) Allow 20 minutes for thermal equilibration in the 15°C bath, then mix the solutions, and commence timing simultaneously. Titrate 10-ml samples at increasing intervals of time between 2 and 150 minutes. (If the greater part of the hydrochloric acid is run into the titration flask before the sample is added, the titration can be completed in a more leisurely way.) The rate constant is determined graphically using the general second-order equation:

$$\frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = kt$$

where $a$ and $b$ are the initial concentrations of sodium hydroxide and ester respectively, and $x$ is the decrease in concentration in time $t$. In this case $a = 2b$. For each time $t$, $(a - x)$ can be calculated directly from $a$ and from the ratio of the titration values at times $t$ and 0. Values of $x$ and of $(b - x)$ are then obtained by subtraction.

*Second kinetic run.* 25 ml of sodium hydroxide solution and 25 ml of aqueous acetone are added to one compartment of the reaction vessel, and 50 ml of ester solution to the other. The subsequent procedure is similar to that in the first experiment. In this case $a = b$, and the rate constant is calculated from the specialized second-order equation:

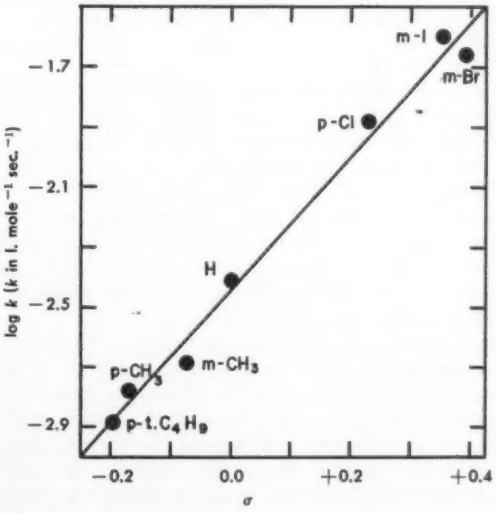
$$\frac{1}{a-x} - \frac{1}{a} = kt$$

The two values of the rate constant should be averaged.

A range of esters must be chosen whose rates can be measured without greatly modifying the above method. Those for which substituent constants are given in Table 1 are suitable. The rate constant increases approximately threefold for an increase in $\sigma$ of 0.2. The procedure for methyl benzoate ($\sigma = 0$) is therefore suitable for all esters with substituent constants in the range −0.2 to 0.2, providing the intervals between titrations are suitably adjusted. For those in the range 0.2 to 0.4 the rate should be reduced by halving the concentrations of alkali and ester. The concentration of the acid titrant must also be halved: the method for methyl benzoate is then followed. Esters with considerably faster or slower rates can be studied if more drastic modifications in the method are adopted, but the scheme suggested is more easily administered and leads to good results.

A constant temperature of 15°C was achieved by running tap water through a metal coil in an otherwise conventional thermostat bath. In warmer regions it would be convenient to choose a higher temperature (up to 25°C) or to use an ice bath. At 25°C the rates are about 2.5 times greater than at 15°C, and esters with substituent constants in the region −0.4 to 0.2 should be chosen. (It is inadvisable to more than halve the reactant concentrations unless precautions are taken to exclude $CO_2$ while titrating). At 0°C the rates are 4 times slower than at 15°C, and the more rapidly hydrolyzed esters up to and including the para-nitrobenzoate ($\sigma = 0.778$) should be used. The abundance of compounds in this range makes 0°C a better choice than 25°C.

If desired the reaction can be followed conductometrically (*1*). In this case the initial concentrations of alkali and ester must be equal.




Student results. ρ (slope of line) = 2.23.

## Results

In the Sheffield laboratory, each student plots his own result (after it has been checked) on a suitably

labelled graph, which is prominently displayed during the period of the exercise. One group's results are shown in the figure. The standard deviation ($S$) and the correlation coefficient ($r$) are then calculated (*11*) as a separate exercise on the statistical treatment of errors. (These calculations are a desirable but by no means essential part of the exercise.) The results in Table 2 correspond to those in the figure: $\rho$, $n$, and log $k_0$ have all been defined. The results quoted by Jaffé were obtained with esters having a wider range of rate constant; but the two sets are otherwise comparable, and experience has shown that results of this standard are normal for the exercise.

**Table 2. Typical Student Results for Hydrolysis of Substituted Methyl Benzoates**

| Source | $\rho$ | $S$ | $r$ | $n$ | $-\log k_0$ |
|---|---|---|---|---|---|
| Present work | 2.23 | 0.077 | 0.991 | 7 | 2.44 |
| Jaffé (*6*) | 2.30 | 0.122 | 0.991 | 10 | 2.45 |

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(*5*) Jaffé, H. H., *ibid.*, 192.
(*6*) Jaffé, H. H., *ibid.*, 191–261.
(*7*) See, e.g., Jaffé, H. H., *ibid.*, 237; Leisten, J. A., *J. Chem. Soc.*, 765 (1959); Leisten, J. A., and Kershaw, D. N., *Proc. Chem. Soc.*, 84 (**1960**).
(*8*) See, e.g., Taft, R. W., *J. Am. Chem. Soc.*, 4231 (1953); Brown, H. C., and Okamoto, Y., *J. Am. Chem. Soc.*, 1913 (1957), and 4979 (1958); Taft, R. W., and Lewis, I. C., *J. Am. Chem. Soc.*, 2436 (1958); Knowles, J. R., Norman, R. O. C., and Rodda, G. K., *J. Chem. Soc.*, 4885 (**1960**).
(*9*) Hammett, *op. cit.*, p. 194.
(*10*) Adapted from Tommila, E., and Hinshelwood, C. N., *J. Chem. Soc.*, 1801 (**1938**).
(*11*) Jaffé, H. H., *loc. cit.*, 253.



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# Polystyrene—A Multistep Synthesis

## *For the undergraduate organic chemistry laboratory*

An unusually stimulating preparative sequence carried out in the second semester organic laboratory is the multistep synthesis of polystyrene, starting effectively from benzene.

Benzene is first acetylated with acetic anhydride. This standard acetophenone preparation is followed by a sodium borohydride reduction to phenylmethylcarbinol (1-phenylethanol).[1,2] The latter is isolated and purified by vacuum distillation. Student yields in the reduction are of the order of 60–65%.

Dehydration of phenylmethylcarbinol with potassium hydrogen sulfate leads to styrene in yields of 70–85%. Attempts to dehydrate the alcohol with sulfuric acid, phosphoric acid, or anhydrous zinc chloride lead directly to polystyrene. If desired the styrene may be purified by vacuum distillation, but in practice the crude monomer is dissolved in an arene, e.g., toluene or xylene, and dried conventionally or by azeotropic distillation (e.g., distillation of about 10% of the solvent or until the distillate is clear); and the solution is used in the next step. In either case, styrene is characterized through formation of the solid adduct obtained by addition of bromine.

The styrene is then polymerized by refluxing its solution in the arene with a small amount of dibenzoyl peroxide. A one hour reflux period is sufficient to give reasonable conversion to polystyrene. The reaction mixture is added to excess methanol and the precipitated polymer isolated by decanting the solvent mixture, filtering if necessary, and triturating the solid with fresh methanol. The final step gives from 2 to 2.5 g of product from an average of 6.5 g of styrene. The conversion depends upon the length of time allowed for reflux.

The sequence requires approximately four 4-hr laboratory periods when benzene is the starting material. If desired, acetophenone may serve as the starting material with a reduction in time of at least one laboratory period. This time can be reduced further by not drying the styrene before polymerization.

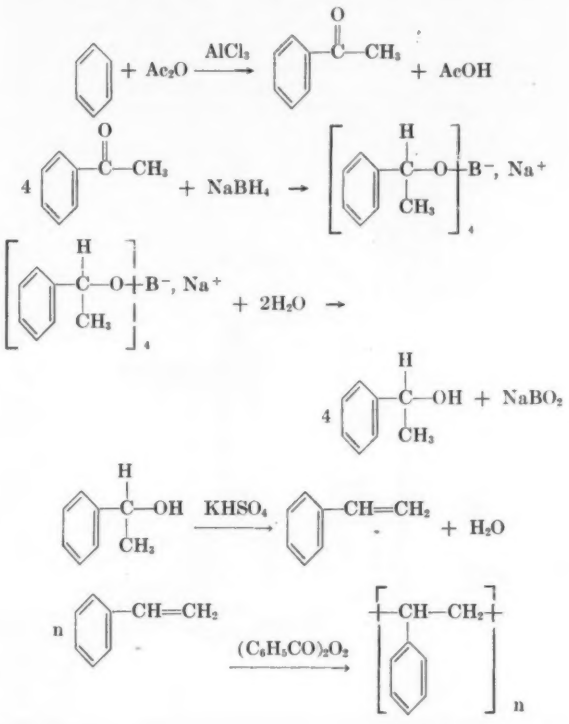
Although the sequence is somewhat lengthy, the time invested in it is felt not to be excessive inasmuch as it exposes students to a wide variety of techniques, reactions, and compounds: Friedel-Crafts acylation,

[1] Chaikin, S. W., and Brown, W. G., *J. Am. Chem. Soc.*, **71**, 122 (1949).
[2] "Sodium Borohydride, Potassium Borohydride," Metal Hydrides Inc., Beverly, Mass., **1958**.

reduction with a metal hydride, dehydration of an alcohol, controlled polymerization, vacuum distillation of an easily dehydrated compound, drying by azeotropic distillation, and trituration.

It may be mentioned that in the authors' classes in which this sequence has been carried out, student interest has been high and good results have been obtained by nearly all students.

The sequence (simplified) is summarized as follows:



## The Experiment

*Phenylmethylcarbinol.* Over a period of approximately 15 minutes, 12.0 g of acetophenone[3] is added by drops to a solution of 1.20 g of sodium borohydride[4] in 25 ml of ethyl alcohol contained in a 125-ml Erlenmeyer flask. The flask is swirled and the temperature is maintained below 50° by external ice cooling if necessary. A white precipitate forms during the course of the reaction.

After the reaction mixture has stood for fifteen minutes at room temperature, a total of 10 ml of a 10% hydrochloric acid solution is added by drops. During the course of this addition, excess sodium borohydride is decomposed with evolution of hydrogen gas and most of the white solid dissolves. The supernatant is decanted, 5 g of solid anhydrous potassium carbonate[5] is added, and the solution is concentrated on a water-bath until two layers are visible in the distilling flask. At this point, most of the ethanol will have distilled.

The two layers (one aqueous, the other consisting principally of the reduction product) are extracted with ether (40 ml total) and the ether extract dried over anhydrous potassium carbonate.

After separation from the drying agent, fresh anhydrous potassium carbonate is added to the ether solution and the ether is removed by distillation on the steam-bath.[6] With the solid potassium carbonate still present,[5] the residue is vacuum distilled from an oil bath, bp 102.5–103.5°/19 mm, 97°/13 mm.

*Styrene.* A mixture of 10 g of phenylmethylcarbinol, 1.0 g of potassium hydrogen sulfate and 0.1 g powdered copper metal[7] is placed in a 125-ml distilling flask fitted with a short condenser. The mixture is distilled from an oil bath whose temperature is gradually (10 minutes) brought up to 200–220°. The vapor temperature should not exceed 130°. The distillate is collected in a 10-ml graduate cylinder. The yield of crude styrene may be estimated from the volume of the organic layer (density of styrene = 0.91) or from the volume of the aqueous layer.

For isolation of the styrene, the organic layer is taken up in 30 ml of ether, the ether extract washed with saturated aqueous sodium carbonate, dried over anhydrous calcium chloride and distilled from copper powder, first on the steam-bath and then under vacuum, bp 48°/20 mm.

If styrene is not to be isolated, the original distillate containing the crude styrene is diluted with three times its volume of toluene or xylene (commercial mixture), the small aqueous layer separated, and the styrene-arene solution dried either over anhydrous calcium chloride or by distillation of the arene until the distillate is clear (distilling 10–20 ml is generally sufficient).

*Polystyrene.* To a solution of styrene in an arene containing approximately 6.5 g of styrene, 0.1 g of dibenzoyl peroxide[8] is added. After refluxing for one hour (longer refluxing leads to a greater conversion), the solution is poured slowly into 150–200 ml of methanol. The methanol is decanted from the white solid material or filtered with suction if necessary. The solid is triturated with fresh methanol until it is tractable, then filtered and dried. A small portion of the polystyrene so prepared may be redissolved in toluene and a film cast by allowing the solvent to evaporate on a glass or metal plate.

*Styrene dibromide (1,2-Dibromophenylethane).* To two or three drops of crude styrene in a test tube there is added a 5% bromine in acetic acid solution until an orange color persists. The orange solution is poured into 5–10 ml of water to precipitate the solid styrene dibromide. The solid is isolated by suction filtration with a Hirsch funnel, washed with cold water, and recrystallized from aqueous ethanol, mp 73°.

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[3] For typical directions see ADAMS, R., AND JOHNSON, J. R., "Laboratory Experiments in Organic Chemistry," 4th ed., The Macmillan Co., Inc., New York, **1949**, p. 311; BREWSTER, R. Q., VANDERWERF, C. A., AND MCEWEN, W. E., "Unitized Experiments in Organic Chemistry," D. Van Nostrand Co., Inc., Princeton, N. J., **1960**, p. 163; VOGEL, A. I., "Practical Organic Chemistry," 3rd ed., Longmans, Green and Co., New York, **1956**, p. 729.

[4] Metal Hydrides Inc., Beverly, Mass. Current price is $10/100 g. The hydride should be kept off the skin, and goggles should be worn when it is handled (see footnote 2).

[5] Traces of acid would result in dehydration of the alcohol.

[6] At this stage, two students usually combine their samples and perform the vacuum distillation together.

[7] Addition of copper powder to the dehydration mixture reportedly reduces the tendency to polymerize; BERGMANN, E. D., AND KATZ, D., *J. Chem. Soc.*, 3216 (**1958**).

[8] It is safer to purchase dibenzoyl peroxide in, and dispense it from, cardboard containers than screw cap jars.

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# Apparatus for the Friedel-Crafts Reaction

## *For the undergraduate organic chemistry laboratory*

The Friedel-Crafts alkylation reaction is a standard experiment carried out in nearly all undergraduate organic laboratory courses. The reaction and its modifications clearly illustrate electrophilic aromatic substitution.

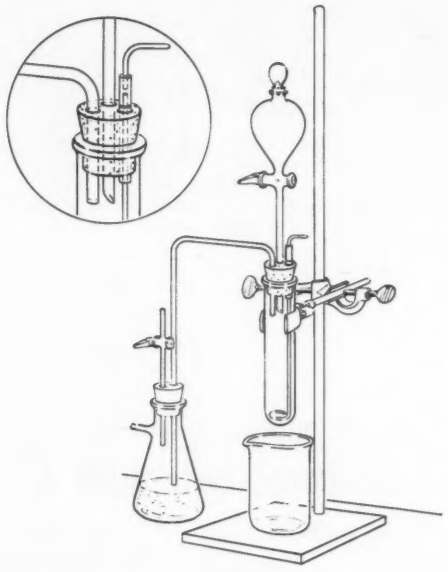
The standard set-up usually employed in Friedel-Crafts alkylations consists of a flask connected to a reflux condenser, with a two-hole cork inserted in the top of the condenser to provide for a dropping funnel and a gas trap takeoff. The heterogeneous reaction mixture is agitated by shaking the entire set-up or by partially breaking the reaction flask away from its connection with the reflux condenser and shaking the flask alone. The first method endangers the gas trap and dropping funnel atop the condenser; the second invites the escape of hydrogen halide gas.

A simple and practical reaction apparatus has been designed which offers the following desirable qualities: compactness and stability, efficient stirring, ease of temperature control, moderate capacity, and an efficient gas trap.

The apparatus consists of a 38 × 200 mm borosilicate glass test tube fitted with a cork holding a dropping funnel, a manual stirrer, and an attachment to a suction flask gas trap. The stirrer is made from 4-mm. glass rod in two pieces held together by a small section of tight-fitting gum rubber tubing. The location of the rubber tubing is such that it prevents the stirring circle from striking the bottom of the tube on a downward stroke. At its point of furthest descent, the stirring circle is within 1/4 inch of the bottom of the tube. The plane of the stirring circle is at right angles to that of the rod shaft. The clearance of the stirring rod through the 7-mm glass tube bearing allows for a rapid up and down motion without the use of a lubricant.

The suction flask serves as a trap for any hydrogen halide gas evolved. The inlet tube terminates about 1/4 inch above the surface of water in the flask. When the apparatus is functioning, slight suction from a water aspirator produces a gentle sweep of hydrogen halide gas from the reaction tube into the trap. None of the gas escapes through the stirrer during a reaction due to this suction. In reactions where no hydrogen halide gas is evolved, as in the preparation of cyclohexylbenzene from cyclohexene, benzene, and sulfuric acid, the gas trap is dispensed with. The dropping funnel is then set in an outside hole of the cork and a thermometer in a center hole if a more accurate measure of the reaction temperature is desired.

Temperature control in many of the alkylations is effected simply by the cooling action of a beaker of ice and water, brought up around the reaction tube when the temperature begins to exceed 30°. An approximate temperature of 30° can be readily noted without the use of a thermometer: it is the temperature that first imparts a sensation of warmth to the touch of the hand. Since most of the alkylations proceed readily below 30° there is no need for a reflux condenser. Refluxing at any stage would probably increase the amount of polysubstitution.



Reaction volumes up to 90 ml are readily accommodated in the large test tube. Good yields are obtained in various alkylations by employing reaction volumes varying between 60 and 90 ml.

The described apparatus has been used successfully in these laboratories for Friedel-Crafts alkylations to prepare:

*Cyclohexylbenzene* from either cyclohexene or chlorocyclohexane reacting with benzene in the presence of either concentrated sulfuric acid or anhydrous aluminum chloride as catalyst.

*Tertiary butylbenzene* from either *tert*-butyl chloride or *tert*-butyl alcohol reacting with benzene and using anhydrous aluminum chloride as catalyst.

*Diphenylmethane* from benzyl chloride and benzene with anhydrous aluminum chloride.

*Tertiary butyltoluene* from either *tert*-butyl chloride or *tert*-butyl alcohol reacting with toluene in the

presence of either anhydrous aluminum chloride or concentrated sulfuric acid as catalyst.

The preparation of *tert*-butylbenzene[1] is described here to illustrate the use of the apparatus and to present a Friedel-Crafts modification that is ideally suited for the undergraduate organic laboratory course.

Prepare the apparatus as shown in the figure. The large test tube, the dropping funnel, and the stirrer assembly must be dry. Place 11 g of powdered anhydrous aluminum chloride and 60 g of dry benzene in the tube. Cork the tube, attach the gas trap, and apply slight suction to the flask from a water aspirator. Now place 12.5 g of dry *tert*-butyl alcohol in the dropping funnel and add it dropwise to the vigorously stirred mixture in the reaction tube. Test for approximate temperature by placing the hand against the reaction tube. If a sensation of warmth is imparted to the hand, cool the tube by surrounding it momentarily with a mixture of ice and water contained in a beaker. Repeat this operation when necessary during the course of the reaction.

After all the alcohol has been added (15–20 minutes), allow the reaction mixture to stand at room temperature, with occasional stirring, for one-half hour.

In a hood, disconnect the reaction tube and carefully pour its contents, with stirring, into a slurry of 50 g of concentrated hydrochloric acid and 50 g of ice. After the ice has melted, separate the benzene and aqueous layers in a separatory funnel, extract the aqueous layer with 25 ml of diethyl ether, and combine the ether extract with the benzene layer. Wash the combined organic solutions with 35 ml of a saturated sodium bicarbonate solution (Caution! Pressure may develop in the separatory funnel due to evolved carbon dioxide gas), separate the organic layer, and wash it with an equal volume of water. Dry the benzene-ether solution over 3–4 g. of anhydrous calcium chloride.

Fractionate the dried liquid and collect the fraction boiling between 165–172° as *tert*-butylbenzene. Yield, 11–14 grams.

[1] Huston, R., Fox, W., and Binder, M., *J. Org. Chem.*, **3**, 251 (1938).

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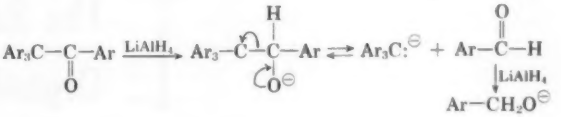
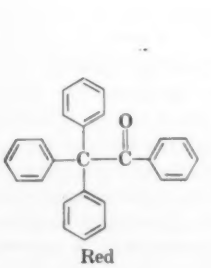
# A Convenient Method for Demonstration of Stable Carbanions

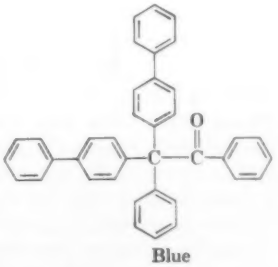
Tangible evidence for the existence of the reactive intermediates in organic chemistry is probably most vividly presented to beginning students by the characteristic colors of the triphenylmethyl carbonium ion, free radical, and carbanion. Whereas the trityl carbonium ion is easily accessible by dissolving triphenylcarbinol in concentrated sulfuric acid,[1] the generation of the carbanion from triphenylmethane by the action of potassium amide in liquid ammonia[1] is less convenient. For facile demonstration purposes, it would be useful to have a higher boiling solvent which does not require special cooling, and a readily available base which can be handled without excessive caution. We now suggest the use of lithium aluminum hydride in pyridine or tetrahydrofuran for the metalation of triphenylmethane and related weak organic acids whose conjugate bases are highly colored in solution.[2] A complementary method for obtaining these carbanions involves cleavage of alkoxides (reversal of carbanion addition to carbonyl groups).

Lithium aluminum hydride in pyridine solution has recently been found to effect the reductive cleavage of benzpinacolone, and certain related ketones, to triarylmethide ion and benzyl alcohol[3], as well as the normal reduction of a variety of other ketones. Thus, highly colored pyridine solutions of carbanions can be obtained instantaneously from the following ketones (colors shown under formula):

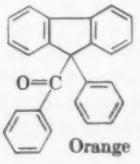




Red



Blue



Orange

[1] Noller, C. R., *J. Chem. Ed.*, **26**, 429 (1949).

[2] Leffler, J. E., "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, **1956**, p. 177.

[3] Lansbury, P. T., *Chem. and Ind.*, **1960**, 151; *J. Am. Chem. Soc.*, **83**, 429 (1961).

Tetra-*p*-methylbenzpinacolone also gives a red coloration. Although these ketones are not all readily available, benzpinacolone is often prepared by beginning organic students as an illustration of the pinacol rearrangement, following the photochemical reduction of benzophenone[4]. Students could thus prepare triphenylmethide at the conclusion of such an experiment. The cleavage of the ketones shown can be observed in tetrahydrofuran also, although product studies confirm that the extent of cleavage is much less than in pyridine.

The basicity of lithium aluminum hydride in pyridine is greater than in ether, as shown by the ability of this combination to metalate triphenylmethane and similar acids.[3] Thus, the following hydrocarbons give intensely colored pyridine solutions when lithium aluminum hydride is added: triphenylmethane (red), fluorene (orange), 4-benzylbiphenyl (violet), 9-phenyle fluorene (orange), di-*p*-biphenylylphenylmethan-(blue), 1-benzhydrylnaphthalene (green). The list of compounds tested is only a portion of potentially useful carbanion sources. By contrast, none of these hydrocarbons are metalated by lithium aluminum hydride in ethyl ether, nor does benzpinacolone undergo reductive cleavage in this solvent. In tetrahydrofuran, fluorene reacts slowly to give the 9-fluorenyl anion.[5]

The reactivity of carbanions generated from either an appropriate ketone or a hydrocarbon is easily demonstrable by the rapid bleaching observed upon addition of oxygen, carbon dioxide, or an alkyl halide.

### Demonstration Procedures

The author has carried out many small scale reductive cleavages and hydrocarbon metalations in stoppered test tubes or Erlenmeyer flasks. To about 0.5–1.0 g of ketone or hydrocarbon in 10 ml of pyridine (dried over barium oxide) is added an equimolar quantity of powdered lithium aluminum hydride (the exact amount is unimportant in the case of demonstrations). The flask is loosely stoppered for a few seconds, while some heat is evolved and the color rapidly appears, then tightly stoppered and kept at room temperature for extended periods, as desired.

To demonstrate the reaction of triphenylmethide with oxygen, it is desirable to use tetrahydrofuran as solvent, in which only a small amount of carbanion forms within 5–10 minutes. The stoppered container can then be shaken so that oxygen present consumes the red anion. The color reappears after the solution is allowed to stand briefly. This cycle can be repeated several times until the red color persists, when all oxygen in the container has been used up. The instructor or student can then note the effect of briefly opening the container to renew the supply of oxygen, then resealing and continuing the demonstration. We have allowed each member of a class of sixty students to observe these phenomena during a lecture, when a test tube containing about 0.1 g of triphenylmethane in tetrahydrofuran with lithium aluminum hydride was passed around the group.

[4] For example, see FIESER, L. F., "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, 1957 p. 165.

[5] TREVOY, L., AND BROWN, W. G., *J. Am. Chem. Soc.*, **71**, 1675 (1949).

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*Introducing students to*

# The Reactive Intermediates of Organic Chemistry

In recent years chemists have become more and more concerned with the paths by which chemical reactions take place. Since many reactions (particularly in organic chemistry) proceed in a stepwise manner, it is obviously important that students become familiar with the structures of possible reaction intermediates fairly early in their chemical education. A consideration of reaction intermediates is *not* the same thing as teaching reaction mechanisms. It is, in fact, an essential prerequisite to that. All of the modern organic texts which have recently appeared make frequent and early reference to reaction mechanisms. Now, one obviously does not discuss the mechanism of the conversion of compound A to compound B until the student is thoroughly familiar with the structural symbols used for compounds A and B. Similarly one should not discuss the mechanism of the conversion of compound D to compound F via some reactive intermediate E until the student has at least some familiarity with the structure of E.

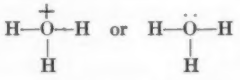
The reactive intermediates of organic chemistry have been the subject of an excellent book[1] but one which is not likely to be seen by many students of organic chemistry until they have been exposed to a great deal of mechanism. The purpose of the present paper is to

[1] LEFFLER, J. E., "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, 1956.

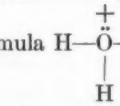
outline a logical but brief presentation of the more important reactive intermediates the student is likely to encounter in organic chemistry. A fairly early discussion of these molecules and ions not only prepares the way for discussion of mechanism but also makes very much easier descriptions of certain resonance structures which involve separation of charge.

The four most important elements to be considered are carbon, nitrogen, oxygen, and halogen, possessing four, five, six, and seven valence electrons respectively. When these atoms possess a share in eight valence electrons (well established by this time in the student's mind as the ideal condition) and are neutral, it follows that they must be bonded by four, three, two, and one covalent bonds, respectively, to other atoms. The atoms in question bear no formal charge because their formal share of one half of the electrons in the bonds plus their own non-bonding electrons adds up exactly to the number of valence electrons each of the neutral atoms possesses. The non-bonding electrons are not usually indicated in the structures but this causes no difficulty since everyone is thoroughly familiar with the numbers of these electrons in such molecules as ammonia (and hence amines and amides) and water (and hence alcohols, aldehydes,etc.).

When one considers possible cationic forms of these four elements, some slight difficulty in symbolism is encountered. One need only write $NH_4^+$ for ammonium ion since there are no non-bonding electrons but if one wishes to indicate the non-bonding electrons in oxonium ion or other, less familiar, oxygen cations, it is necessary to use the symbol



It seems to be considered in poor taste to designate such



ions by the formula H—Ö—H, possibly because of the implication that the reader is not capable of telling what the charge is if only the bonds and electrons are shown or (alternatively) what the number of spare electrons is if only the charge and number of bonds is shown; and possibly because of the jarring effect on the eye of the juxtaposition of electrons and positive charge in the formula. A bracket around the electron formula and the charge placed thereon is sometimes possible, but this cannot always be done with more complex ions in which it is important that the location of the charge on a particular atom be specified. In Table 1, which gives the bonding types for the anions, cations, and radicals of carbon, nitrogen, oxygen, and halogen, the non-bonding electrons are designated. In Tables 2 and 3, which give some typical molecular structures, the commonly used method is followed; i.e., the number of bonds to a given atom and the charge, if any, on the atom are shown. It is obviously most important that the student be able to recognize by inspection the number of non-bonding electrons on any atom in a molecular formula.

**Table 1. Bonding to Carbon, Nitrogen, Oxygen, and Halogen Atoms**

| | C | N | O | X |
|---|---|---|---|---|
| Number of valence electrons | 4 | 5 | 6 | 7 |
| Anion | —C⁻— | —N⁻— | —O⁻: | :X: |
| | Increasing Stability → | | | |
| Cation | —C⁺— | —N⁺— | —O⁺— | —X⁺— |
| | ← Increasing Stability | | | |
| Neutral radical | —Ċ— | —Ṅ— | —Ȯ: | :Ẋ: |

### Anions and Cations

If we consider the anions possible for the four elements carbon, nitrogen, oxygen, and halogen, we find that each can have a share in eight electrons in the anionic state provided that the number of bonds are three, two, one, and zero, respectively (Table 1). The order of stability of these ions is exactly what would be expected from electronegativity considerations, i.e.

$$X^{\ominus} > -O^{\ominus} > -\overset{|}{N}^{\ominus}- > -\overset{|}{C}^{\ominus}-$$

When one considers the cations, however, we find that only nitrogen, oxygen, and halogen can be cationic and have a share in eight valence shell electrons. Carbon cannot do this without expanding its valence shell beyond eight electrons and using higher energy orbitals. The number of bonds to cationic nitrogen, oxygen, and halogen are four, three, and two, respectively, and the

$$-\overset{|}{N}^{+}- > -O^{+}- > -X^{+}-$$

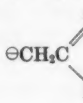
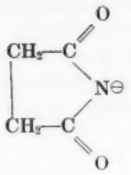
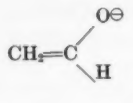
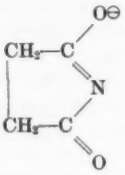
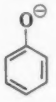
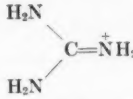
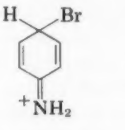
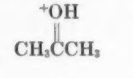
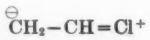
order of stability is again exactly what would be expected from electronegativity considerations. Carbon can only be cationic if it has *three bonds* and *no unshared electron* pairs and hence has a share in only *six* electrons. It thus follows that carbonium ions (positively charged) and carbanions (negatively charged) are both going to be rather high energy species (unless specially stabilized by, for example, resonance) but for different reasons: carbanions because of the low electronegativity of carbon and carbonium ions because of the electron deficient valence shell, i.e. the atom has a share in only six valence electrons.

### Radicals

The situation with the radicals of carbon, nitrogen, oxygen, and halogen is somewhat different, as might be expected. Here each of the central atoms has a share in seven valence electrons and is neutral. All of these radicals are met fairly frequently in chemistry. Since they carry no formal charge electronegativity effects will be small and they might be expected to have comparable stabilities, as in fact they do.

Table 2 shows typical structures of the cations, anions, and radicals of carbon, nitrogen, oxygen, and halogen. Included in this table are contributing

**Table 2. Typical Structures for the Anionic, Cationic, and Radical Forms of Carbon, Nitrogen, Oxygen, and Chlorine***

| | C | N | O | Cl |
|---|---|---|---|---|
| Normal neutral forms | $CH_4$ | $NH_3$ | $H_2O$ | HCl |
| Anionic forms | $(C_6H_5)_3C^{\ominus}$  | $NH_2^{\ominus}$  | $OH^{\ominus}$    | $Cl^{\ominus}$ |
| Cationic forms | $(C_6H_5)_3C^+$ | $NH_4^+$   | $H_3O^+$  | $H_2Cl^+$  |
| Radical forms | $(C_6H_5)_3C\cdot$ | $(C_6H_5)_2N-\dot{N}-C_6H_2(NO_2)_3$ | $(CH_3)_3C-O\cdot$ | $Cl\cdot$ |

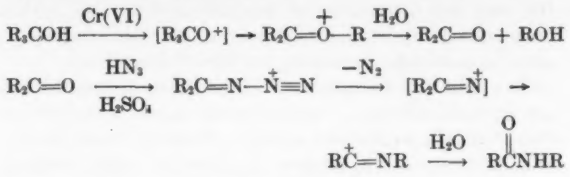
* Certain of the structures shown here are minor contributing structures in a resonance hybrid, and indeed the same ion appears in some cases in different places in the table.

structures to resonance hybrids as well as those in which the charge is localized on particular atoms. The relative importance of the contributing structure to a resonance hybrid also varies according to the electronegativity of the atom in question.

### Electron Deficient Systems

Since a carbonium ion has only six valence electrons, unlike all the other ions in Tables 1 and 2, it should really be compared to the electron deficient forms of nitrogen, oxygen, and halogen. The term electron deficient is frequently used to describe any ion or molecule with only six electrons in its outer shell.

If we compare the stabilities of carbonium ions to those of the electron deficient cations of nitrogen, oxygen, and halogen, we find now that carbonium ions are clearly the most stable. The electron deficient ions $\diagdown C=N^+$ and $R-O^+$ are often written as reaction intermediates, as in the following examples; but it is probable that they never exist as fully formed, discrete ions since the 1,2-shift which is a part of each reaction is believed to be synchronous with ion formation. This in itself is an indication that the electron deficient cations of nitrogen and oxygen are of very high energy.



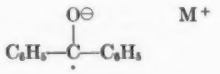
The much greater stability of carbonium ions can be attributed to two factors. First, carbon is less electronegative than nitrogen or oxygen and a positive charge will be borne better by that atom. Second, the carbon atom in a carbonium ion can be attached to three different groups, each of which (in the case of stable ions) can interact with the central carbon atom by resonance and hence stabilize the ion.

In Table 3 are listed examples of electron deficient cations and neutral molecules. Except for the lone oxygen atom, only carbon and nitrogen can be neutral and still have a share in but six electrons. The molecule of structure is an intermediate in the Hofmann hypobromite reaction, but even here the 1,2-shift may be synchronous with the formation of this electron deficient species. Carbenes are becoming familiar reaction intermediates and it is reasonable to suppose that they too undergo 1,2-shifts in those cases where this structural change is possible. Throughout this discussion of electron deficient species we have not been concerned with the question of their multiplicity, i.e. whether they are singlet (non-radical) or triplet (diradical) molecules and ions.

### Ion-Radicals

Ion-radicals possessing both an odd electron and a charge are, of course, capable of existence. Removal of an electron from an ordinary compound will produce a species which is both a radical and a cation. Addition of an electron will, conversely, produce an anion-radical. They are simply radicals with an excess or deficiency of protons. The semiquinone anions like I, below, are well-known examples of anion-radicals as are the metal ketyls (II) produced by the donation of an electron by a metal atom to a ketone.

I



II

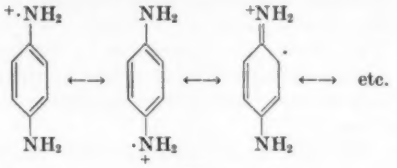
In the former, both the negative charge and the odd electron are shared by both oxygen atoms and all the carbon atoms in the ring. In the ketyl anion-radical, the negative charge will prefer to be chiefly on the oxygen atom leaving the unpaired electron on carbon, although the resonance structure with this reversed undoubtedly contributes to the resonance hybrid.

A stable cation-radical is produced by the oxidation of *p*-phenylene-diamine with bromine in acid solution.

Table 3. Typical Structures for the Electron Deficient Forms (Six Valence Electrons) of Carbon, Nitrogen, Oxygen, and Chlorine

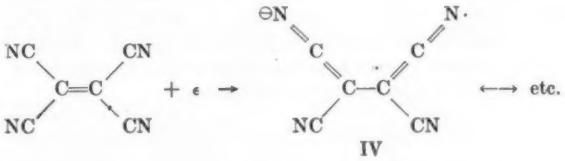
| | C | N | O | Cl |
|---|---|---|---|---|
| Neutral forms | $CH_2$ <br> $CH_3-\overset{\overset{O}{\|}}{C}-CH$ | $CH_3-\overset{\overset{O}{\|}}{C}-N$ | O | ... |
| Cationic forms | $(C_6H_5)_3C^+$ etc. | $CH_3-\overset{\overset{O}{\|}}{C}-\overset{+}{N}H$ | $(CH_3)_3C-O^+$ | $Cl^+$ |

Highly colored products of this type, which are analogous to semiquinones, are called Wurster's salts (III) and as with virtually all stable ion-radicals a very large number of resonance structures can be written.



III

Tetracyanoethylene will remove an electron from various unsaturated molecules to become an anion-radical, IV:



IV

It should be pointed out that the Wurster's salt ion-radical (III) differs in a formal way from the semiquinone oxygen ion-radical (I) and the tetracyanoethylene ion-radical (IV). The oxygen atoms in I and the nitrogen atoms in IV are bonded in the manner shown in Table 1. That is, I and IV are ion-radicals because one of the atoms in each molecule is a radical and another bears a charge, i.e., is ionic. (Each equivalent atom by virtue of resonance bears both the charge and the odd electron, of course). In the Wurster's salt ion-radical (IV) however, the charged atom is the one which possesses the odd electron.

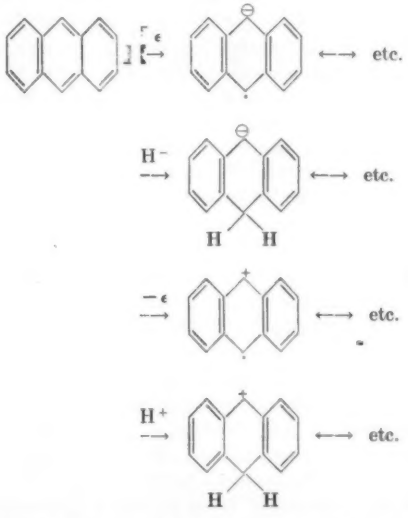
Table 4 shows the bonding arrangement possible for the four elements under discussion when the atom in question itself bears both an odd electron and a charge. The oxygen ion-radical arrangement shown there will be infrequently met, since the high electronegativity of oxygen will tend to destabilize the oxygen cation-radical arrangement (two bonds and one odd electron) and since a true oxygen anion-radical is not possible

Table 4. The Ion-Radical Bonding Arrangement for Carbon, Nitrogen, Oxygen, and Chlorine Atoms

| | C | N | O | Cl |
|---|---|---|---|---|
| Cation ($\dot{+}$) | ... | $-\dot{N}-$ | $-\dot{O}-$ | $-\dot{Cl}:$ |
| Anion ($\dot{-}$) | $-\dot{C}-$ | $-\dot{N}:$ | $:\dot{O}:$ | ... |

if any group is bonded to the oxygen. Carbon atoms bearing both a charge and an odd electron will likewise be very rare since the low electronegativity of carbon will make the only possible structure, a doubly-bonded anion, of very high energy.

The relation between the structures of carbonium ions, carbanions, cation-radicals, and anion-radicals can be illustrated by considering the reaction of anthracene with reagents which will do these four things: (*a*) add an electron to produce an anion-radical (sodium in ether will accomplish this), (*b*) add a hydride ion to produce a carbanion (lithium aluminum hydride might be expected to do this but it has been observed that a very high temperature is required to reduce anthracene with this reagent), (*c*) remove an electron to form a cation-radical (sulfuric acid acting as an oxidizing agent produces this species), and (*d*) add a proton to form a carbonium ion (a non-oxidizing acid such as hydrogen fluoride accomplishes this).



In the case of the ion-radicals above, the charge and/or odd electron can be distributed by resonance to all positions in the rings. In the case of the carbonium ion and the carbanion, the charge can be located on seven of the ring carbons.

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# Electronic Configuration of Metal Oxides

The oxides of metals exhibit a wide range of electrical, optical, magnetic, and chemical characteristics. A useful classification of these interesting solids can be made into "closed shell" oxides which may be considered to be formed from oxide ions $O^=$ and metal ions with a filled electronic shell and oxides of the transition-, lanthanum- and actininum-series of metals for which the constituent metal ions do not have a completed electronic shell. Of the latter type of oxides only those of the first transition series of metals will be discussed in this paper.

The energy band theory (*1*) of solids, which has been rather successful in the explanation of the properties of metals and valence crystals such as silicon and germanium, appears to be applicable to metal oxides, although a complete interpretation of the properties of metal oxides by band theory has yet to be made. The magnitude of the energy gap between the uppermost filled band (oxygen $2p$) and lowest empty band of oxides depends sharply on the type of metal forming the oxide. Available values of the energy gap, $E_g$, of closed shell oxides indicate that $E_g$ decreases sharply with decrease in the electronegativity difference (*2*) $\Delta\chi$ between the metal and oxygen. $E_g$ also varies with the value of the principal quantum number $n$ of the valence electrons of the free neutral metal atoms from which the oxide is derived. The variation of $E_g$ with $\Delta\chi$ for closed shell metal oxides of the fourth row of the periodic table ($n = 4$) is shown in Figure 1. Although these oxides have different crystal structures and hence differ in energy band structure, the dependence of $E_g$ on $\Delta\chi$ parallels the increase in covalent character (*2*) of the corresponding metal–oxygen bonds with decrease in $\Delta\chi$. Values of $E_g$ are derived from the temperature variation of electrical conductivity or the position of the optical absorption edge of the solid. The thermal values of $E_g$ often differ somewhat from the optical values—where both values are available tney are indicated in Figure 1.

Closed shell metal oxides may thus be subdivided into insulators such as MgO and $Al_2O_3$ and semiconductors such as ZnO and PbO. Oxides of metals of the first transition series behave as insulators, semiconductors, and in some cases, as metals, due to the presence of the incomplete shell of $3d$ electrons.

The classical theory of ionic solids of Born and Mayer has been applied to metal oxides and yields rather good agreement between observed and calculated values of lattice energy (*1*). Although such agreement does not prove that metal oxides are completely ionic (since the Born-Mayer theory yields good results even for solids such as PbS which are considered to be rather covalent), it does indicate that, as a first approximation, metal oxides can be considered to consist of metal ions and oxide ions.

In the following section, crystal field theory (*3*) is discussed and applications to thermodynamic, optical, and paramagnetic properties of metal oxides are illustrated. A description of properties of metal oxides which are due to covalency, such as antiferromagnetism and electronic conduction, is then given. Next, the chemical catalytic properties of metal oxides and their relationship to covalency are considered. In conclusion, a brief discussion of problems in an energy band description of metal oxides is presented.

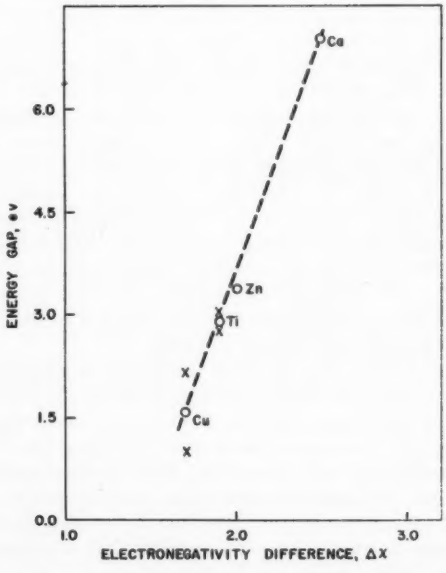


**Figure 1. Energy gap $E_g$ between uppermost filled band and lowest empty band of closed shell oxides of fourth row metals versus electronegativity difference between metal and oxygen. X represents optical or thermal value of $E_g$, o represents arithmetic average of optical and thermal values of $E_g$. The value of $E_g$ for Ca is estimated.**

## Crystal Field Theory

A $3d$ valence electron of a metal ion of the first transition series has an orbital angular momentum of $2\hbar$ (Planck's constant/$2\pi$), i.e., $l = 2$, and an intrinsic

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or spin angular momentum equal to $(1/2)\hbar$, i.e., $s = 1/2$. As a result, there are $(2l + 1) = 5$ different orbitals for such an electron and $(2s + 1) = 2$ different spin orientations for each orbital. In a metal ion with one $3d$ electron, such as $V^{+4}$, all of these orbitals have the same energy in the gaseous ion, not in chemical combination. When the ion is in chemical combination, however, the $3d$ orbitals no longer are energetically the same, but differ in energy due to their directional properties. Consider a $3d$ electron metal ion surrounded by an octahedral array of oxide ions, as frequently occurs in metal oxides. As shown in Figure 2, two of the five orbitals, designated by $e_g$, are higher in energy than the remaining three, designated by $t_{2g}$. The reason for such splitting of the free ion $3d$ electron level is apparent after examination of the distribution of electron probability amplitude for each orbital, also

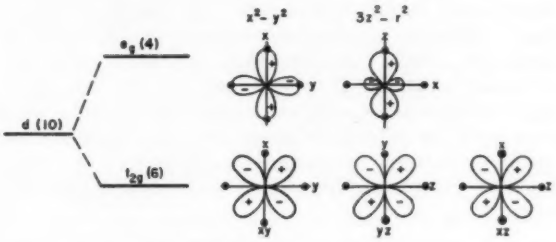


**Figure 2. Energy levels of a single *d* electron and contours of constant probability amplitude of *d* electron wave functions.**

shown in Figure 2. The $e_g$ orbitals point in the direction of the oxide ions and overlap them considerably, while the $t_{2g}$ orbitals, on the other hand, are directed between the oxide ions and overlap them much less than do the $e_g$ orbitals. Due to greater electrostatic repulsion, therefore, the $e_g$ orbitals are higher in energy than the $t_{2g}$ orbitals. Denoting the energy of the $e_g$ orbitals by $E_e$ and that of the $t_{2g}$ orbitals by $E_t$, it is necessary that when both the levels are filled with electrons the total energy, relative to the unsplit $3d$ level, is zero. That is

$$4E_e + 6E_t = 0 \qquad (1)$$

Denoting the energy separation $E_e - E_t$ by 10 $Dq$, one finds $E_e = +6\ Dq$ and $E_t = -4\ Dq$. The quantity $Dq$ is an empirical parameter which may be obtained from the optical spectra of transition metal oxides.

For dipositive metal oxides of the first transition series of metals, the $3d$ electrons occupy the $e_g$ and $t_{2g}$ levels so as to have maximum total spin. Thus if three electrons are in the $t_{2g}$ levels, the fourth would go into the $e_g$ level and not until the sixth electron is added will the $t_{2g}$ orbital be occupied by four electrons. The total energy of the $3d$ electrons is called the stabilization energy $\delta H$ and is given by

$$\delta H = (4n_t - 6n_e)Dq \qquad (2)$$

where $n_t$ and $n_e$ are the number of electrons in the $t_{2g}$ and $e_g$ orbitals, respectively. For metal oxides $Dq$ is in the range of 0–6 kcal/mole, so that the stabilization energy can be as high as 10% of the total lattice energy. For the $d^2$ and $d^7$ configurations $n_t$ and $n_e$ are generally not integers unless $Dq$ is sufficiently large (*3*).

For some tripositive metal ions in oxides, such as $Co^{+3}$, it is a better approximation to consider that the electrons fill all the lower $t_{2g}$ orbitals before occupying the $e_g$ orbitals, since $Dq$ is large (*4*). However, in this strong crystal field or low spin approximation, the energy required to pair electrons must be included. For the configurations $d^1$, $d^2$, $d^3$, $d^8$, and $d^9$ the low spin approximation is the same as the high spin approximation, but for $d^4$, $d^5$, $d^6$, and $d^7$ the crystal field configurations differ in the low and high spin approximations. These situations are illustrated for various cobalt(II) and cobalt(III) compounds in Figure 3.

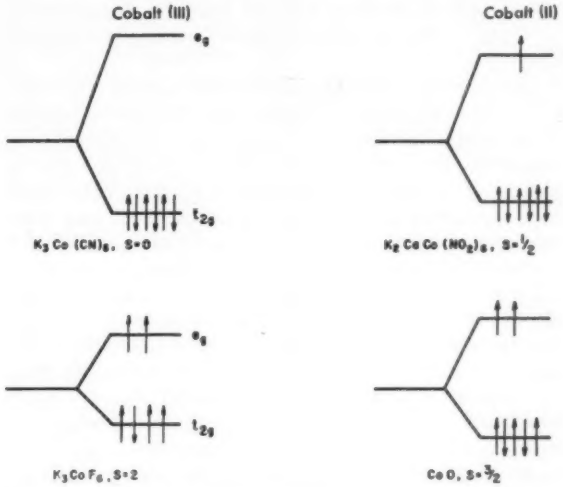


**Figure 3. Low and high spin compounds of cobalt. The 3*d* energy levels are simply represented by the levels for octahedral coordination. Electron occupation of levels and spin orientation in levels is indicated by arrows.**

The thermodynamic stabilization energies (*4*) of dipositive $3d$ metal oxides are given in Figure 4 and compared with values of the stabilization derived from

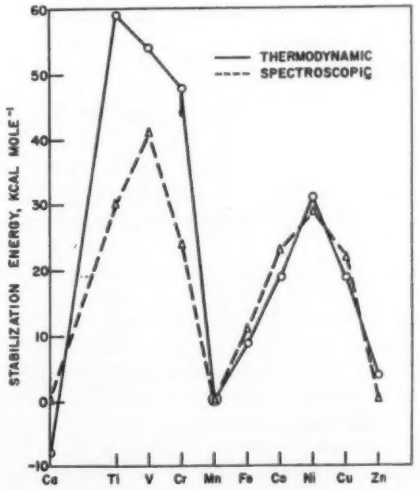


**Figure 4. Thermodynamic and spectroscopic stabilization energies of dipositive metal oxides of the first transition series of elements.**

spectroscopically determined values of $Dq$. The thermodynamic stabilization energy is computed from the experimental lattice energy of a dipositive oxide by

subtraction of the lattice energy computed from the Born-Mayer theory. That is,

$$\delta H = U_{\text{expt}} - U_{\text{L}} \tag{3}$$

where

$$U_{\text{L}} = \frac{Ae^2}{r_0}\left(1 - \frac{1}{n}\right) \tag{4}$$

$A$ is the Madelung constant, $r_0$ the sum of the ionic radii (*2*) of the metal ion $M^{+2}$ and $O^{-}$ and $n$ is the exponent of $1/r$ in the repulsive potential. All the oxides given in Figure 4 are simple cubic ($A = 1.748$) except CuO which has the tenorite structure ($A \approx 1.645$) and ZnO which has the wurtzite structure ($A = 1.641$). For all these oxides $n$ is taken to be equal to 8.0.

The spectroscopically derived $\delta H$ values are computed from $Dq$ values derived from the optical spectra of the oxides and hydrated metal ions in solutions using equation (2), assuming the electrons occupy the $t_{2g}$ and $e_g$ levels so as to produce maximum total spin. The agreement between the thermodynamic and spectroscopic stabilization energies is good and is indicative of the correctness of the crystal field theory.

Ions of transition metals may be substituted into closed shell oxides and by their optical and, in particular, magnetic properties act as probes by which details of the electronic structure of the host oxide may be ascertained; for example, consider the ion $Cr^{+3}$ which has $3d$ electrons and a ground state crystal field configuration of $(t_{2g})^3$. The configuration $(t_{2g})^2$ $(e_g)$ in which one electron is removed from the $t_{2g}$ level and placed in the $e_g$ level gives rise to two energy levels $^4T_1$ and $^4T_2$ depending on whether the $e_g$ electron is in the $3z^2 - r^2$ or $x^2 - y^2$ orbitals. The configuration $(t_{2g})$ $(e_g)^2$ gives rise to a single energy level. These levels are illustrated in Figure 5. Thus the optical spectrum of $Cr^{+3}$ in an octahedral crystal field shows three absorption bands—generally two are in the visible and one in the ultraviolet.

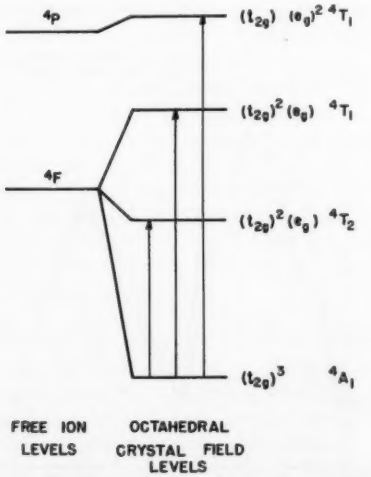


**Figure 5. Energy levels of $Cr^{+3}$ in a cubic octahedral crystal field. Arrows denote possible electron transition.**

In addition to the broad bands due to quartet-quartet transitions, weak, sharp absorption bands are observed, caused by transitions from the quartet ground state to excited doublet states in which two electrons in the $t_{2g}$ or $e_g$ orbitals have opposite spin orientation. These transitions also give rise to sharp emission bands, which have attracted much attention.

The technique of electron paramagnetic resonance (EPR) perhaps is the most useful in the study of the magnetic properties of closed shell oxides doped with transition metal ions. The EPR absorption of a single crystal of MgO with a few tenths per cent of chromium impurity shows that three types of chromium are present (*5a*): (1) $Cr^{+3}$ ions in a pure cubic crystal field giving rise to a single, intense resonance line with weak hyperfine structure from $Cr^{+3}$, (2) $Cr^{+3}$ ions in a crystal field of axial symmetry with the symmetry axis along the (100) type directions, and (3) $Cr^{+3}$ ions in a crystal field of rhombic symmetry with symmetry axes in face-diagonal (110) type directions. Chromium of type (1) is due to $Cr^{+3}$ substituted for $Mg^{+2}$ with no associated lattice vacancy in the vicinity. Type (2) chromium is interpreted as type (1) chromium with a $Mg^{+2}$ vacancy in the next-nearest cation position along the (100) type directions. Finally, type (3) chromium is similar to type (1) but with an associated $Mg^{+2}$ in the nearest-neighbor cation sites [(110) directions]. Thus direct evidence for the presence of crystal vacancies is supplied. Paramagnetic resonance of $F$-centers in irradiated MgO has also been observed (*5b*).

### Effects of Covalency

By the use of the technique of EPR, effects due to the covalency of metal oxides can be directly observed. This is illustrated by the spectrum of $Mn^{+2}$ in MgO at a concentration of about 0.2% Mn. As is well known (*6*), an extensive pattern of resonance lines is observed corresponding to a $g$-factor of 2.00 and due to isolated $Mn^{+2}$ ions substituted for $Mg^{+2}$. Six main lines result for $Mn^{+2}$ in a cubic site, since $Mn^{55}$ has a nuclear spin $I = 5/2$ and there are $2I + 1 = 6$ different orientations of the $Mn^{55}$ nucleus for which the $3d$ electrons experience a different local magnetic field due to hyperfine interaction. There is a further additional splitting of the ground state energy level of $Mn^{+2}$ ($S = 5/2$) in a cubic crystal field which results in 6 unequally spaced electron spin levels in a magnetic field and hence 5 lines in the absence of the nuclear hyperfine interaction. In total, therefore, there are $5 \times 6 = 30$ lines which appear, not all of which are resolved due to the relatively high $Mn^{+2}$ concentration.

In addition to the intense lines due to isolated $Mn^{+2}$ ions, weak lines consisting of eleven hyperfine components are observed (*6*).

Upon rotation of the Mn-doped MgO relative to the applied magnetic field, the intense pattern remains in the vicinity of 3400 gauss while the eleven line pattern moves to various field strengths. Two types of 11-line patterns are observed (*6*), one of which is ascribed to Mn-O-Mn pairs occupying next-nearest-neighboring sites and the other to Mn-Mn pairs occupying nearest-neighbor cation sites. The spectra observed correspond to $S = 1$ and 11 lines result from the two $Mn^{55}$ nuclei with a total spin of 5. This situation would result if the $Mn^{+2}$ pairs are coupled by an exchange interaction which favors the antiparallel arrangement of

spins, so that the lowest state would correspond to $S = 0$ or parallel spins and successive excited states have $S = 1, 2, 3, 4,$ and 5.

The $Mn^{+2}$ electron spins are coupled by the so-called superexchange interaction. This coupling of electrons results from overlap of $e_g$ and $t_{2g}$ $d$ electron orbitals with the oxygen $2p\sigma$ orbitals (for Mn-O-Mn) and $2p\pi$ orbitals (for Mn-Mn), respectively. Since the two electrons of an oxygen $2p\sigma$ (or $\pi$) orbital are paired, the Mn-O overlap results in opposite spin orientation for both nearest and next-nearest neighbors of a given $Mn^{+2}$ ion, due to the spin correlation between these Mn neighbors produced by electronic overlap with the oxygen $2p$ electrons.

The superexchange interaction results in the phenomena of antiferromagnetism (no net magnetic moment) in metal oxides and ferrimagnetism( partial magnetism) in mixed transition metal oxides or metal oxides in which the metal exists in two valence states (e.g., $Fe_3O_4$ or $Mn_3O_4$). Above a definite temperature, referred to as the transition or Néel temperature, transition metal oxides are paramagnetic; below the transition temperature the oxides are antiferromagnetic or ferrimagnetic as the case may be. Available transition temperatures for divalent metal oxides are given in Table 1. It is of interest to note that $T_c$ increases with decrease in ionic radius (*2*) of the metal ion, except for $Cu^{+2}$ which does not have the rock salt structure, but rather the tenorite structure in which two of the six oxygens surrounding the metal ion are further from the metal than the other four. This relationship of $T_c$ and $R$ reflects the increase in metal-oxygen overlap with decrease in metal radius.

**Table 1. Transition Temperatures and Ionic Radii of Divalent Metal Oxides of the First Transition Series**

| Oxide | $T_c$ (°K) | Radius (Å) |
|---|---|---|
| TiO | <10 | 0.90 |
| VO | 120 | 0.88 |
| CrO | ... | 0.84 |
| MnO | 116 | 0.80 |
| FeO | 190 | 0.76 |
| CoO | 291 | 0.74 |
| NiO | 520 | 0.72 |
| CuO | 230 | 0.74 |

The effect of the transition from the paramagnetic to the antiferromagnetic state is quite striking in the EPR spectra of a sample of $\alpha$-$Cr_2O_3$ at various temperatures (*9*). The resonance at temperatures above the transition temperature (~33°C) is a symmetrical line, which disappears at temperatures below about 30°C, due to the onset of spin alignment in $Cr_2O_3$.

In the stoichiometric state the dipositive oxides of Mn, Fe, Co, Ni, and Cu are insulators or weakly semiconducting (*7*). However, the dipositive oxides of Ti and V exhibit metallic conductivity above $T_c$ and become semiconductors with a small energy gap below $T_c$. MnO, FeO, CoO, NiO, and CuO are considered to have well localized $3d$ electrons in $t_{2g}$ and $e_g$ orbitals, as inferred from their poor conductivity. In TiO and VO, on the other hand, the $e_g$ and $t_{2g}$ levels are considered to be broadened into bands. Above the transition temperature band conduction occurs in the $t_{2g}$ band, below the transition temperature conduction is impeded by the tendency for the spins to be oriented relative to one another and be localized on cations. For VO, the $t_{2g}$ band is only half filled above the transition temperature so that metallic conduction occurs.

The oxides MnO, FeO, CoO, NiO, and CuO, when nonstoichiometric or doped with oxides of monopositive metals such as $Li_2O$, show $p$-type semiconductivity (*8*). When doped with $Li_2O$, $M^{+3}$ ions are produced in the lattice so as to compensate for the $Li^+$ ions which substitute directly for the dipositive metal. In these doped oxides, the electrical conductivity due to the metal ion holes is not via a conduction band, but rather proceeds by diffusive migration of the holes through the lattice. The activation energy for hole conduction is overcome by optical mode lattice vibrations which free the trapped hole for migration after which it again becomes trapped on a $M^{+2}$ ion and so on. The diffusion coefficient of the electron hole is proportional to the amount of copositive character of the oxide, i.e., the overlap between adjacent metal ions.

### Chemical Catalysis

The copositive properties of metal oxides are manifested in the chemical catalytic properties of metal oxides. A frequently used catalytic method is to support catalytically active $3d$ metal oxides on relatively inert closed shell metal oxides such as $Al_2O_3$. Reference 9 gives EPR spectra of samples of differing amounts of chromia supported on $\gamma$-alumina. Unpaired electrons in three different types of environment are apparent: (1) $Cr^{+3}$ ions which are not strongly coupled via exchange interactions with other $Cr^{+3}$ ions as evidenced by the maximum of the absorption derivative in the vicinity of 1500 gauss, (2) $Cr^{+3}$ ions strongly coupled to other $Cr^{+3}$ ions by the exchange interaction giving rise to the symmetrical absorption derivative centered near 3400 gauss, and (3) unpaired electrons which give rise to a relatively sharp absorption at $g = 1.973$ which appears when the chromia is partially oxidized and appears to correspond to electrons trapped on $Cr^{+6}$ ions, i.e., $Cr^{+5}$. When the sample is oxidized at low temperatures an unsymmetrical resonance appears which is ascribed to $O_2^-$ ions adsorbed on the surface of the solid. Chromium of type (2) above dominates at the higher total chromium concentrations and appears to be most active for catalysis of the dehydrogenation of saturated hydrocarbons. The chromium associated with electrons of type (3), on the other hand, appears to be most active in the decomposition of hydrogen peroxide.

Variation of catalytic activity with number of $3d$ electrons of transition metal oxides is very strikingly made apparent by the data of Dowden, MacKenzie and Trapnell (*10*) on the rate of exchange of hydrogen and deuterium over oxides of the first series of transition metals. These data are given in Figure 6. It is of interest that the activity is "twin peaked" in the interval $3d^0$ to $3d^{10}$.

The significance of this twin-peaked activity pattern may be qualitatively understood from crystal field theory by reference to Figure 7. Here the approximate splittings of the $e_g$ and $t_{2g}$ energy levels upon the removal of one of the six coordinating ligands to form a square pyramid are given. A somewhat similar situation must exist on the clean surfaces of metal oxides in that the metal ions are not completely coordinated

with ligands. If now the surface is exposed to hydrogen, $H_2$ molecules will be adsorbed on the surface of the metal oxide. It is assumed that one end of the $H_2$ molecule coordinates with the incompletely coordinated

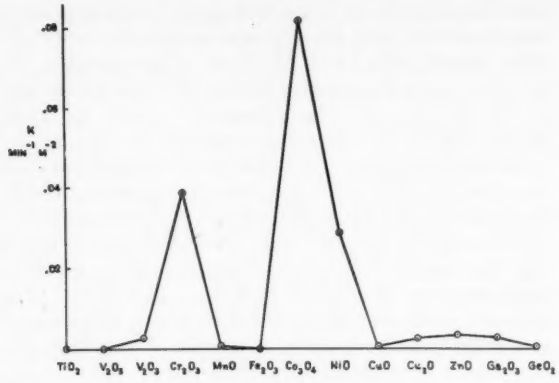


Figure 6. $H_2$-$D_2$ exchange activity over metal oxides (*10*).

metal and the other end interacts with oxygen resulting in the induction of a dipole moment in the molecule. With reference to Figure 7, one can show that the transition from the square pyramidal coordination to octahedral is exothermic only for the configurations $d^3$ ($V^{+2}$, $Cr^{+3}$) and $d^8$ ($Ni^{+2}$) and also $d^6$ ($Co^{+3}$) (in the low spin approximation) so that for these configurations adsorption of hydrogen would appear to be

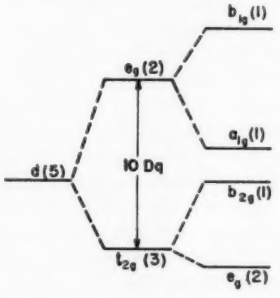


Figure 7. 3*d* electron energy levels in crystal fields of octahedral and square pyramidal coordination.

favored. Desorption can occur by conversion of the ion to which the hydrogen is attached to one for which the original conversion of the square pyramid to octahedral coordination is endothermic. This can result by electron or hole diffusion from the solid to the adsorption site. Isotopic exchange can occur by desorption of different pairs of hydrogen atoms from adjacent sites. Under reducing conditions, the only oxides of Figure 6 for which the above conditions for high activity are met are $V_2O_3$ ($V^{+2}/V^{+3}$), $Cr_2O_3$ ($Cr^{+3}/Cr^{+2}$), $Co_3O_4$ ($Co^{+3}/Co^{+2}$) and NiO ($Ni^{+1}/Ni^{+1}$) where the adsorption-desorption oxidation states are given in parentheses. Thus a qualitative understanding of the $H_2$–$D_2$ exchange activity of transition metal oxides results from consideration of crystal field stabilization energy and electron and hole mobility in an oxide lattice.

### Energy Band Theory

The usual energy band description of solids (*1*) assumes that the motion of the atoms in the crystal influences the energy states of the bonding electrons to only a small degree. In oxides, particularly those of the transitional metals, this assumption does not appear to be valid, in that strong interactions between lattice vibrations and electronic motions occur (*11*). Furthermore, as evidenced by the antiferromagnetic properties of transitional metal oxides, strong correlational effects between electrons result so that localization of electrons of definite spin orientation on cation sites occurs. Future calculations of the band structure of these oxides will have to consider these important effects.

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# Electrochemistry of the Solid State

The site of reaction in any electrochemical cell is the phase boundary at which electronic conduction changes to electrolytic conduction and *vice versa*. Conduction electrons are consumed or produced by these processes. The most commonly encountered boundaries are those between a metal and an aqueous solution or between a metal oxide and an aqueous solution. Electrochemists have tended to take as their special region of investigation that part of the cell extending from the interface (including any adsorbed species) into the solution, while as a matter of fact processes occurring on the other side of the boundary, that is, in the solid itself, often play a dominant part in determining the behavior of the electrochemical cell. Methods and concepts of solid state physics and chemistry are very useful to the chemist who desires an understanding of these processes, and many of them can be described quite satisfactorily by means of the rudimentary theory of solids.

We will consider here a few of the phenomena of electrochemistry in this way to illustrate the application of solid state theory.

Initially we treat the general electrochemical cell, comparing the electronic energy levels in the metallic and electrolytic portions of the cell and showing that a significant part of the electromotive force arises from levels in the metals. We then consider the behavior of oxide electrodes to include the growth of oxide layers, the rectifying action of tantalum and aluminum oxides, and the polarization and recuperation of primary cell "depolarizers." Cells utilizing solid electrolytes are next described.

Finally, we must illustrate quite a different aspect of the connection between electrochemistry and solid state theory: the use of electrochemical methods in the development of the theory itself. This aspect is best exemplified by transport number measurements in crystals.

## Electronic Levels and Potentials in Cells

An electrochemical cell is diagrammed, in a general form, in Figure 1. Letters indicate different phases. The external portion may be a detector, free space, a conductor, or an additional source of electromotive force (emf); or it may be eliminated by joining the two sections of $A$ together. For complete generality it is not required that $A$, $B$, and $C$ be metals, but they must be electronic conductors. $A$ is included so that the potential difference measured by an external detector will be that between two points located in media of identical composition (*1*). Alternatively either $C$ or $B$ could replace the two sections of $A$.

When the current $I = 0$, the cell is said to be an emf cell only. When $I \neq 0$, the cell is both an emf cell and an electrolysis cell. The first condition is achieved in practice when the external portion is free space, a detector of very high resistance, or an opposing source whose emf equals that of the cell.

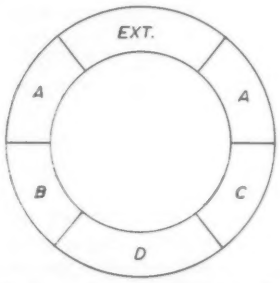


**Figure 1. The generalized emf cell. "EXT" represents all parts of the circuit external to the cell and leads.**

The emf of the cell arises from potential differences across the phase boundaries. The potential difference across the $A$–$B$ boundary, for example, we write as $e_{A-B}$ and imply by this notation the change in potential passing from $A$ to $B$. Upon taking the sum of all phase-boundary potential differences in the circuit, observing that all boundary-crossings must be made in the same direction (e.g., counterclockwise in Figure 1), and adding the emf arising in the external portion, we have

$$e_{A-B} + e_{B-D} + e_{D-C} + e_{C-A} + e_{\text{ext.}} = IR$$

where $R$ is the total resistance of the circuit. If $I$ is made zero by adjustment of $e_{\text{ext.}}$, the emf of the cell is given by

$$e_{\text{cell}} = -e_{\text{ext.}} = e_{A-B} + e_{B-D} + e_{D-C} + e_{C-A}$$

Now, the potential difference between two metals in contact is not altered if a third metal is interposed between the two. This is a consequence of thermodynamic law governing the behavior of electrons in metals as will be shown in the next section. Thus $e_{C-A} + e_{A-B}$ is just $e_{C-B}$, and the use of metals other than the electrodes for connectors has no effect on the

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cell emf. Thus we find that the cell emf is

$$e_{cell} = e_{B-D} + e_{D-C} + e_{C-B}$$

that is, it is composed of the two electrode-electrolyte potentials and the *contact* or *volta potential*,[1] which would result on bringing the two electrodes into contact. Three is the minimum number of phase boundary potentials in an electrochemical cell.

Whether the emf of galvanic cells arises at the metal-metal interface or at the sites of electrochemical reaction was a question which gave rise to a lively controversy lasting well over a century. Volta discovered the potential difference which bears his name in 1797; on separating two pieces of metal which had been brought into contact, he found that they bore opposite charges. He believed that the contact potential between metals was responsible for the emf of his voltaic pile. Three years later Ritter found that the action of the pile was accompanied by chemical changes, which he concluded were the cause of the emf. For many years the Peltier emf was confused with the contact potential; when it was shown by LeRoux in 1866 that the Peltier emf was small, most chemists were convinced that Ritter was substantially correct. However, both Kelvin and Helmholtz argued correctly that the Peltier emf was not equal to the contact potential, $V$, but rather to $T(\partial V/\partial T)$. Kelvin (*2*) supported the contact theory of Volta and devised a way to measure contact potentials directly. Unfortunately, all early measurements were subject to serious errors from surface contamination; the reality of a sizable contact potential was as doubtful as ever. Not until experiments were carried out with metals having really clean surfaces in high vacuum could it be proven that the contact potential was indeed a significant part of, but not solely responsible for, the emf of electrochemical cells. The account of this historic dispute was reviewed by Langmuir (*3*) shortly after it was finally settled.

### The Contact Potential

The contact potential between two metals, which we have seen is one of not less than three phase-boundary emf's, arises from differences in electronic levels in the metals. Metals contain nearly free electrons, which occupy a set of closely spaced energy-levels. Because of the Pauli principle, there can be only two electrons (one of each spin) in each level in a given sample of metal. The levels are filled from the lowest level upward until the electrons are exhausted. The occupancy of levels is governed by the Fermi-Dirac statistics; at room temperature essentially all the levels up to a quite definite energy (the Fermi energy) are filled, and those above this energy are empty[2]. Figure 2a depicts the situation in two metals before being brought into contact. $E_F$ denotes the Fermi level in each case. Upon contact, electrons flow from the higher levels in metal $B$ into $C$, equilibrium being established when the new Fermi levels become equal. The Fermi energy can be shown to be the electronic chemical potential, so that it is clear that Figure 2b represents the equilibrium situation. As a result, metal $B$ is charged positively with respect to $C$; the electrical double layer gives rise to a potential difference. Its magnitude is just the difference in original Fermi energies per electron.

It is now clear why we were able to replace $e_{C-A} + e_{A-B}$ by $e_{C-B}$. Writing the contact potentials as the differences between Fermi levels of the metals before contact, we have

$$e_{C-A} + e_{A-B} = E_{F_A} - E_{F_C} + E_{F_B} - E_{F_A} = E_{F_B} - E_{F_C} = e_{C-B}$$

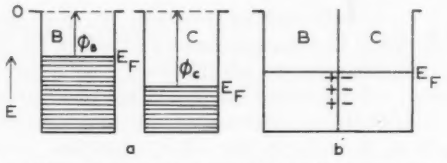


**Figure 2. Electronic levels in two metals (a) before contact and (b) after contact. Work functions, $\phi$, are shown in (a).**

The energy at the Fermi level, relative to the energy of an electron at rest in a vacuum outside the metal, is given by the work function, $\phi$. Figure 2a shows that

$$e_{C-B} = E_{F_B} - E_{F_C} = \phi_C - \phi_B$$

where $\phi$, as is customary, is measured in a positive direction from the Fermi level to the vacuum level. Experimentally, contact potentials are found either by taking the difference between work functions, or by direct measurement (*1*, *4*). At present, the work function of a metal is often measured by directly determining its contact potential against a metal of accurately known work function, usually tungsten.

Table 1 compares the standard emf of several cells with the contact potential of the two metal electrodes.

**Table 1. Cell emf and Contact Potential for Certain Pairs of Metals (in volts)**

| Cell | $e^0_{cell}$[a] at 25° | Work function,[b] Left | Right | Contact potential[c] |
|---|---|---|---|---|
| Cu\|Cu$^{++}$\|\|Ag$^+$\|Ag | 0.46 | 4.5 | 4.3 | −0.2 |
| Zn\|Zn$^{++}$\|\|Hg$^{++}$\|Hg | 1.62 | 3.7 | 4.5 | 0.8 |
| Na\|Na$^+$\|H$^+$,H$_2$, Pt | 2.71 | 2.3 | 4.2[d] | 1.9 |
| Fe\|Fe$^{++}$\|\|Cd$^{++}$\|Cd | 0.04 | 4.4 | 3.9 | −0.5 |

[a] Neglecting liquid junction potential.

[b] Average of values tabulated by MICHAELSON, H. B., *J. Appl. Phys.*, **21**, 536 (1950) except for Pt.

[c] Negative sign indicates contact potential is opposed to $e^0_{cell}$.

[d] For Pt with adsorbed $H_2$. OATLEY, C. W. (*4*). Oatley gives for clean Pt, $\phi$ = 5.4. There is considerable disagreement between published values.

It is clear that the contact potential is a considerable part of the cell emf in these cases, many times acting in the same direction as the cell emf but not infrequently opposed to it. The strongly electropositive elements have low work functions; their highly negative standard electrode potentials are due largely to this circumstance. For other metals there is not a close correspondence between work function and standard electrode potential, as solution-metal boundary potential differences are often sufficient to obscure the

[1] These are actually *potential differences;* when the meaning is clear from the context, the term *potential* is usually used.

[2] Actually there is a narrow energy range within which the occupancy falls from one electron per level to none. The energy at which the probability of occupancy is 0.5 is the Fermi energy.

contact potential of the metal against platinum.

The variation of potential in the cells

$$Na \mid Na^+ \parallel H^+ \mid H_2, Pt^3 \text{ and } Fe \mid Fe^{++} \parallel Cd^{++} \mid Cd$$

both equipped with copper leads, is shown in Figure 3. Note that sodium, which is considered to be the negative electrode, is strongly positive with respect to the copper wire connected to it. The effect is to make this copper wire negative with respect to the wire attached to the platinum electrode. The potential of the solution, with respect to the electrodes, is not known accurately. It may be estimated from measurements of the potential of the dropping mercury electrode at the electro-capillary maximum, and lies at about the position shown by the dotted line in the figure. The

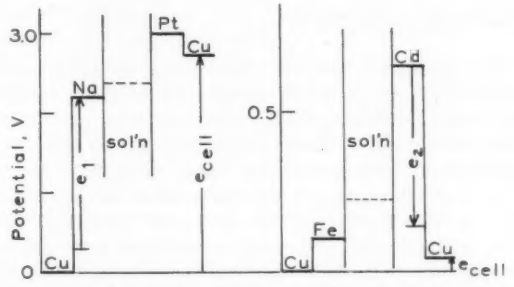


**Figure 3. Potentials in two emf cells. $e_1$ = Contact potential difference Pt — Na. $e_2$ = Contact potential difference Cd — Fe.**

combined potential differences between the solutions and the two metals render platinum 0.8 volt more positive than sodium. It will be noted that in the iron-cadmium cell, the contact potential acts in such a direction as to make the right-hand copper wire negative, whereas the combined potential differences at the solution-metal boundaries are sufficient to overcome the contact potential and render the right-hand copper wire 0.04 volt positive with respect to the left.

A further consequence of importance concerns the use of the hydrogen-platinum electrode as a primary standard. The standard electrode potential of every electrode contains the contact emf of that electrode against platinum which has been saturated with hydrogen. When we compute cell emf's by taking the difference in potential of two electrodes, the Fermi energy of platinum is cancelled, and we are left with the contact emf for the junction between the two electrodes themselves (plus the solution-metal potential differences). Thus, although we might expect a different set of standard electrode potentials if a reversible hydrogen electrode using a metal other than platinum were chosen as a reference standard,[4] cell emf's would be unchanged.

[3] This cell cannot, of course, be realized in the standard state due to direct chemical reaction.

[4] It is not clear what effect the change of metal would have. If the boundary between hydrogen gas and platinum behaved as a metal-metal boundary with respect to contact emf, substitution of another metal for platinum would not alter the standard electrode potentials. This, however, is unlikely. No experimental test can be made, as no other hydrogen gas electrode is even approximately reversible.

### *Levels in Ions and Solvent*

It is instructive to consider what levels exist for electrons in the ions and solvent comprising the electrolyte. Although the electrolyte is generally a liquid, we may profitably consider an electrolyte as the approximate analogue of an insulating solid having localized levels in the band gap, taking account, where necessary, of the high degree of mobility of ionic carriers in the liquid state. It is the transfer of electrons from the Fermi level in the electrodes to localized levels in the electrolyte (or *vice versa*) that accounts for the potential differences $e_{B-D}$ and $e_{D-C}$ of the previous section.

We may assume that the Fermi levels of the electrodes lie too far below the conduction levels of the electrolyte for electrons to be transferred from the electrodes to the electrolyte, and too far above the valence levels of the electrolyte for transfers in the reverse direction, which would result in hole conductivity. The charge transfer only takes place by means of electrochemical action.

## Oxide Electrodes

Oxide electrodes constitute a particularly interesting class of electrochemical cell components, since electronic and ionic transport both may make important contributions to electrode processes.

### *Growth of Oxide Layers*

The formation of oxide layers on the metals aluminum, tantalum, titanium, tungsten, and zirconium is important in the technology and theory of electrolytic condensers, rectification, metal finishing, and corrosion prevention. When aluminum (for example) is made the anode in ammonium borate solution, an adherent resistive layer of aluminum oxide grows to a thickness limited by the applied voltage. Above about 600 volts dielectric breakdown occurs; at this voltage the film has reached a thickness of a few thousand angstroms.

$Al_2O_3$ is essentially an insulator; however, electronic conduction occurs and at sufficiently high fields $Al^{+++}$ ions contribute to conduction. In fact, the layer could not grow, once it had been started, were it not for ionic transport through the layer.

Charlesby (*5*) applied a theory first proposed by Mott (*6*) to account for the oxidation of aluminum in air. Experimentally, the ionic current density $i_+$ in the layer during electrolysis depends on the field, $F$, as

$$i_+ = Ae^{BF}$$

where $A$ and $B$ are constants. Mott considered that the ion had first to surmount an energy barrier of height $U$ and half-width $a$ in order to pass from the metal into the oxide. This leads to the following relation between the ionic current density and the field, as can be observed by noting the effect of the field in Figure 4:

$$i_+ = N\nu q \exp\{(aqF - U)/kT\}$$

Here $N$ is the number of ions per cm$^2$ situated next to the boundary, $\nu$ the vibrational frequency, $q$ the charge on the ion, $k$ Boltzmann's constant, and $T$

the absolute temperature. This equation may be identified with the empirical result for electrolysis by making the substitutions

$$N\nu q \exp(-U/kT) = A \text{ and } aq/kT = B$$

From the empirical values of $A$ and $B$ and reasonable estimates of $N$ and $\nu$, $U$ turned out to be about 1.6 ev and $a$ about 3 A. Since at least part of the oxide was $\gamma$-$Al_2O_3$, which has one vacant cation site for every 8 cations, it is not likely that any considerable activation energy would be required to put the $Al^{+++}$ ion into the oxide; therefore the barrier probably represents activation energy required to extract the ion from the metal.

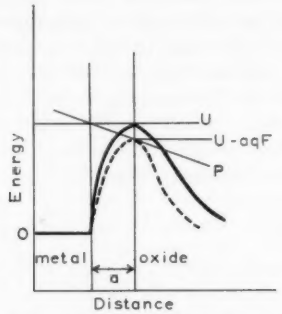


**Figure 4. Effect of field on activation energy for removing ion from metal to oxide.**

The layer thus grows, not at the metal, but at the oxide-solution interface, where $Al^{+++}$ ions and hydrated oxide ions neutralize each other. Electronic conductivity in the oxide is unimportant for this process.[5]

Vermilyea (*7*) concluded that the Mott-Cabrera theory did not apply in the case of the anodization of tantalum. The growth of oxide films on zirconium has been studied by Johansen, Adams and Van Rysselberghe (*8*), and by Young (*9*).

### Rectification

Many attempts have been made to account for the rectifying action of oxide films on tantalum and aluminum electrodes but as yet no satisfactory theory has evolved. The resistivity of the films is much less when the electrodes are cathodes than when they are anodes. Early theories were largely based on the porosity of the films to $H^+$ and $OH^-$ ions; the $H^+$ ions were supposed to pass quite freely through the film to be discharged on the metal when a cathode. When it was the anode, $OH^-$ ions could not easily pass through the film to be discharged, nor could electrons, and $Al^{+++}$ ions could not pass out toward the solution. A theory of rectification applying the band concept of solids, was recently proposed by Smith (*10*). This scheme applies to a voltage range below the formation voltage of the film, so that ionic conductivity may be neglected in comparison to electronic. During passage of current in the "forward" (easy) direction, holes are injected into the valence band from $H^+$ ions in solution; in the "reverse" direction, current is carried by electrons injected into the conduction band from $OH^-$ ions. The rate of electron injection, with the production of $O_2$, was presumed to be much less than the rate of hole injection, so that reverse current is much smaller. The rectifying properties of a germanium-solution interface have been so explained (*11*).

However, more recent experiments by Smith (*12*) and others (*9*, *13*) in which the roughness of the metal surface has been varied, seem to indicate that the rectifying properties are closely related to the occurrence of structural defects such as voids, channels, and inclusions, in the films. Just how such defects give rise to rectification is unknown.

It must be concluded that the cause of rectification in oxide films is still uncertain.

### Oxide Cathodes in Cells

The cathodes (positive electrodes) of most useful voltaic cells are oxides of metals in one of their higher states of oxidation; the most common are $MnO_2$, $PbO_2$, and $Ni_2O_3$. These oxides are still referred to as *depolarizers*, because of the idea, prevalent at one time, that hydrogen gas was the product at the cathode and was depolarized by the action of the oxide. The three oxides named, and others which show some promise as cathode materials, are all semiconductors. The reduction of the oxide during discharge therefore must take place at the interface between the oxide and the electrolyte, not between the metal or carbon used as a connector and the oxide, since the field in the semiconductor is too low to cause appreciable ionic migration.

As current is drawn, oxide cathodes undergo a progressive loss of electrode potential (polarization); on disruption of the current the potential rises rapidly at first, and then more slowly toward the initial value (recuperation). This process is quite marked in $MnO_2$, and affects the closed circuit voltage, intermittent-use voltage, and capacity of the common dry cell operated under various conditions of load and rest. The polarization and recuperation processes in $MnO_2$ will be described in some detail because of their importance in technology and because of the amount of study which this electrode has received, but it must not be assumed that processes which occur in $MnO_2$ are necessarily characteristic of oxide cathodes in general.

There is good evidence (*14*) that the principal reaction occurring during the discharge of $MnO_2$, provided the electrolyte $p$H is not excessively low nor the current density too high, is

$$MnO_2 + H^+ + e = MnOOH$$

Further, it is of course to be expected that the potential of MnOOH is less positive than is that of $MnO_2$ in the same electrolyte; in fact Johnson and Vosburgh (*15*) studied the potential of electrodes made by mixing and sintering $MnO_2$ and MnOOH and found that they followed, at 25°C, the equation

$$E = E_0 + 0.07 \log \frac{N_{MnO_2}}{N_{MnOOH}}$$

where $N$ = mole fraction, and $E_0$ is the potential for

[5] It must be remarked, however, that in the oxidation of aluminum in air, electrons must penetrate the oxide, passing from the Fermi level of the metal into oxygen levels, thus establishing the field in which the ions then move, according to Mott's theory.

$N_{MnO_2} = 0.5$. The multiplier 0.07 differed somewhat from the theoretical value of 0.059, probably due to departure of the sintered mixture from an ideal solid solution.

However, the lattices of $MnO_2$ and MnOOH are sufficiently similar that incorporation of a proton on every second oxygen does not involve much distortion. As the electrode is discharged, protons are brought into the $MnO_2$, and neutralized by electrons which move through the conduction band. If these protons are unable to diffuse into the bulk of the oxide the surface will soon correspond to the composition MnOOH, and the potential will fall to that characteristic of the oxy-hydroxide. However, if the protons, accompanied by electrons moving through the conduction levels, are able to diffuse away fairly rapidly the potential will not fall so rapidly. In addition, on discontinuing the current, the diffusion of protons away from the surface will cause the potential to rise again toward, but never completely to, the initial value.

This mechanism is sketched in Figure 5. The observed polarization and recuperation follows a curve such as *A* of Figure 5. Recently (*14*), it was found possible to reproduce the essential features of this curve by assigning arbitrary, but reasonable, values to the current density and the diffusion coefficient for protons, and calculating the electrode potential as a function of discharge time and recovery time with the aid of diffusion theory. *B* is the curve so calculated. It appears likely that, at least in the case of $MnO_2$, a high diffusivity of protons as well as high electron mobility is necessary in order that an oxide cathode is to be free from objectionable polarization, and recuperate rapidly after cessation of current.

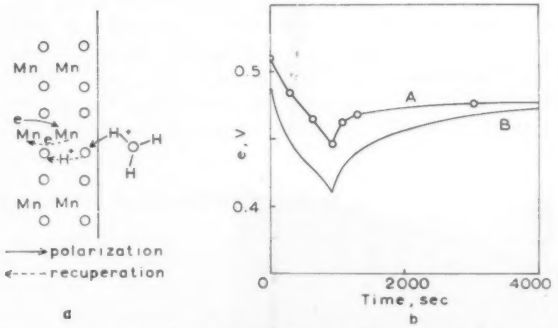


**Figure 5. (a) Mechanism of polarization and recuperation of $MnO_2$. (b) Line *A* = observed polarization and recuperation (discharge stopped at 900 sec), after Ferrell and Vosburgh (*16*). Line *B* = calculated polarization and recuperation.**

## Solid Electrolytes

The most direct application of solids to electrochemistry is in the development of cells having crystalline electrolytes. Such cells are *dry cells* in the strictest sense. Several schemes for high-temperature fuel cells have been devised in which the electrodes are oxides of iron or nickel and the electrolyte is a solid carbonate or vitreous "solid" through which transport is usually by sodium ions. The internal resistance is high, however, even at high temperature, and since the primary purpose of fuel cells is power generation, this presents a serious obstacle in the way of eventual application.

There are, however, some distinct advantages to be obtained from the use of solid electrolytes in cells and batteries. Size and weight can be drastically reduced, and shelf-life increased to as much as 20 years. Since the internal resistance is high at ordinary temperature, application must be limited to drain of less than one microampere; this is, however, a common application in transistorized circuits. Coupled with the increased life, whether under load or not, and capability for miniaturization, solid electrolyte cells are sure to see increased development and use in missile devices.

Consider, for example, the $Ag|AgCl|Cl_2$ cell (*17*). Figure 6 is a schematic diagram of such a cell. The AgCl solid electrolyte is formed on the inside of a silver outer can (negative) by treating with $Cl_2$ for 30 minutes at 200–300° C; the coating is then only a few microns thick. The positive material is a mixture of $KICl_4$, carbon, and grease. $KICl_4$ provides $Cl_2$ at a low pressure, the carbon provides electrical contact to the tantalum lead-wire, and the grease serves as a binder. The top of the can is sealed tightly with teflon.

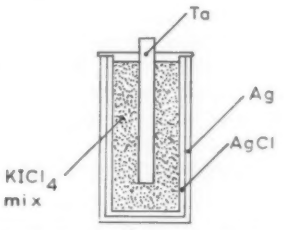


**Figure 6. Solid-electrolyte primary cell.**

Solid AgCl conducts by migration of $Ag^+$ ions present (*18*) as Frenkel defects, but at room temperature the number of defects and their mobility is extremely low. The internal resistance of a cell made as described above is about $10^6$ Ω, and the open circuit voltage is 1.04 volt. Weininger (*19*) has described a similar cell in which the electrolyte is α-AgI, the modification stable above 147° C. The conductivity of this salt is exceptionally high, since the number of available $Ag^+$ sites in a unit cell greatly exceeds the number of $Ag^+$ ions, so that the ions move readily with no requirement for generation of vacancies by thermal energy. The normal operating range is of course limited to temperatures above 147° C.

## Transport Numbers in Crystals

As an illustration of the application of an electrochemical technique which has contributed a great deal to the understanding of ionic crystals, we conclude by reviewing the determination of transport numbers in solids. In the first place, such numbers are important because they tell whether conduction is electronic or ionic. If the sum of all ionic transport numbers is accurately unity, conduction is electrolytic; if it lies between zero and unity, conduction is partially electronic. If all ionic transport numbers are zero, conduction is electronic.

The following method is chiefly due to Tubandt and his colleagues; it can be seen to be an adaptation of the familiar Hittorf method, with the modification that the "electrolyte compartments" are individual crystals and that mass changes instead of concentration

changes are measured. Figure 7 represents a simplified form of the experimental arrangement used by Tubandt, Rindtdorff and Jost (*20*) to determine transport numbers in cuprous iodide. The total charge passed was measured by means of a silver coulometer. After electrolysis the cathode and *A* were weighed together,[6] and *B*, *C*, and the anode were weighed separately. Table 2 gives the results of experiments at two temperatures.

**Table 2. Transport Numbers, *n*, in Cuprous Iodide**

| Temp. °C | Ag deposited, (g) | Cu equiv., (g) | Change in mass, (g) | $n_{Cu^+}$ | $n_{I^-}$ | $n_e$ |
|---|---|---|---|---|---|---|
| 306 | 0.0581 | 0.0342 | Cathode +*A*: 0.0110 | 0.315 | 0.000 | 0.685 |
| | | | *B*: 0.0000 | | | |
| | | | *C*: 0.0000 | | | |
| | | | Anode: −0.0110 | | | |
| 400 | 0.1168 | 0.0688 | Cathode +*A*: 0.0689 | 1.000 | 0.000 | 0.000 |
| | | | *B*: 0.0000 | | | |
| | | | *C*: 0.0000 | | | |
| | | | Anode: −0.0689 | | | |

At 400° the current is essentially entirely electrolytic, and $Cu^+$ ion is the charge carrier. If $I^-$ contributed to transport, crystal C would gain in mass. At 306°, where the ionic mobility is much less, electronic conductivity is relatively of more importance; $n_e$, the electronic transport number, here is 0.685.

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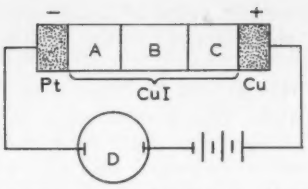


**Figure 7. Determination of transport numbers in solid CuI. *D* is a silver coulometer.**

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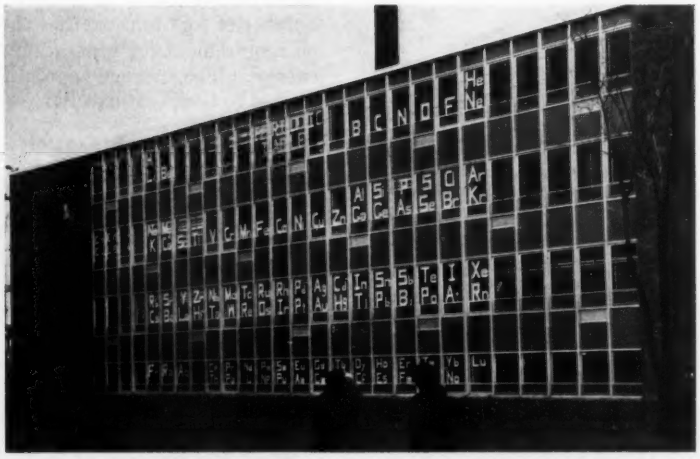

Members of the Chemistry Club at Wisconsin State College, Superior, were dissatisfied with the periodic charts which hung at the front of the Chemistry classrooms. As a result, the side of the Science Building recently blossomed out with what club members believe is one of the largest (if not *the* largest) periodic charts extant. The 2-foot letters were cut from white paper and taped to the inside of the windows.

*Proceedings of the*

**California Association of Chemistry Teachers**

**A. H. Sporer**
International Business Machines Corporation
San Jose, California

# The Role of Chemistry in Computers

Chemists are relying more and more on computers to solve problems which tax human patience and human capability. But another fact about chemistry and computers is less generally known: Computer manufacturers are relying increasingly on chemists for solutions to certain problems related to computer development. These problems involve not so much a set of requirements determined by present computer needs as a series of open questions raised by future computer possibilities. Research in chemistry could conceivably improve computers, and might revolutionize them; but the search itself serves a more general purpose as it uncovers new information and encourages awareness of scientific interdependence.

To those of us in research, this interdependence is obvious and urgent now; more general recognition of this fact will eventually help industry as much as it helps science. Progress in science and technology depends on common efforts by chemists, physicists, and other scientists in laying claim to the "no man's land" where the different sciences overlap and where any one science alone is inadequate. Common efforts among scientists are under way, as evidenced by news of interdisciplinary conferences and cross-disciplinary publications. Such efforts may be seen in current computer research.

### Computers in Chemical Research

Consider first, by way of introduction, the more familiar side of the subject—the role of computers in chemistry. Computers help the chemist in two distinct ways: They save his time in solving relatively straightforward but tedious problems; and they enable him to attack new problems too complex for solution by other means. A look at some typical problems of each kind will suggest some reasons for the chemist's appreciation of computers.

Fitting a line to a number of points by the least squares method—a relatively trivial yet common kind of problem—involves calculations which are highly repetitive but almost exorbitantly time-consuming without mechanical assistance. Even with a desk calculator, hours of work are necessary. But with a computer, the answer is available almost immediately.

Another example: Computers have made numerical analysis a practical way of handling the integration of differential equations. In physical chemical problems, one can often write a differential equation describing, for instance, the successive rates of reaction of a polymerization mixture; but the integration of the equation rapidly becomes unmanageable, and one must make approximations to reach a solution. Attempted manually, these approximations involve a lengthy process; but numerical analysis, performed mechanically, can find the shape of the curve with relative speed and ease. To accomplish this, the computer requires only the boundary conditions for the problem and the incremental step, $\Delta X$, to be evaluated numerically. The $\Delta X$ chosen may be so small that even a fast computer cannot quickly solve the problem to the degree of precision desired; but in principle, numerical analysis is always possible.

Computers also make possible the solution of new kinds of problems, as in X-ray crystallography, where the application of computers to chemistry has been most successful. X-rays of known wavelength, sent through a crystal, are diffracted by the ordered atoms which act as a three-dimensional diffraction grating. When the rays reach a photographic plate or film positioned behind the crystal, a diffraction pattern of the crystal is visible in the form of spots of varying intensity. Any experimental technique used to detect the X-ray diffraction pattern from a crystal determines the intensity of a diffracted spot. The intensity observed at each spot is related to the sum of the diffracted waves from various atoms in the crystal, reaching that spot with various positive and negative amplitudes (i.e., phases). Since the intensity of a wave is the square of the resultant wave amplitude, the sign of the wave (negative or positive) is lost in the experimental determination of intensity. Without this information it is not possible to deduce the structure of the crystal from the diffraction pattern.

The ability of the X-ray crystallographer is taxed to the utmost at this point. He must now assume, by induction, a "reasonable" atomic structure for the crystal. With the computer, he then simulates the X-ray diffraction pattern that would be produced by the assumed crystal structure and compares the simulated diffraction pattern with the actual pattern. By a series of such successive approximations, discarding erroneous assumptions, the actual crystal structure is obtained.

To help him make these "reasonable" approximations, the X-ray crystallographer incorporates a

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"heavy" atom in the crystal structure whenever possible, since it scatters the X-rays much more effectively than the other atoms can and thus produces easily identifiable spots in the diffraction pattern. These spots are all assigned the same phase relationship; and then it is materially simpler to determine a probable structure and to make reasonable approximations. With this technique, it has become possible to determine a structure as complex as that of vitamin $B_{12}$ with more than sixty carbon atoms and one (heavy) cobalt atom.

More recently, however, the X-ray crystallographer has begun to enlist the computer even in the work of making the necessary reasonable approximations. That is, the computer can be used to make a statistical analysis of spot intensities and to correlate the intensities with the respective atoms of differing atomic number assumed to be present, and possibly with their wave phase.

With these computer techniques, it may be possible in the future to determine the structure and configuration of almost any polymer or protein. Biophysicists are becoming increasingly aware that the spatial configuration and the chemical structure of a particular protein are equally important in biological processes. Since X-ray crystallography determines both structure and configuration, it is a powerful tool for the biological sciences.

As these examples suggest, many chemists who have no direct contact with computers are nevertheless aided in their work by data obtained through various applications of computers to chemistry problems. It is obvious that computers relieve the chemist of drudgery and enable him to learn more than he once thought he could know. And appropriately enough, some of the very facts the chemist is learning with the aid of computers may be applied directly to the improvement of these machines.

## Chemical Research for Computers

Historically, computer development has not depended heavily on chemistry. Mechanical, electrical, and electronic engineers have successively taken the lead in designing increasingly complex business machines, with no more than marginal help from chemists. As the machine technology advanced from the manual key punch to the digital computer, and as the business market broadened to include general purpose data processing equipment, certain trends became apparent in the kind of improvements required by the customer and produced by the manufacturer. The changes generally increased the speed of machine operation to handle vast computations within reasonable times, without raising power consumption or lowering mechanical reliability. In recent years, the emergence of electronics provided the principal basis for these improvements in speed and capacity.

The single event most responsible for drawing chemistry into participation in computer research was the introduction of the transistor, which marked a major change in computer development and in technical progress generally. Faster, more compact, and requiring less power than the vacuum tube it replaced, the transistor recommended itself strongly to computer manufacturers. This solid state device made it theoretically possible to increase the speed and complexity of computer operation while decreasing the size of the machines.

This possibility led to intensive study of the semiconductor materials from which transistors are made. Computer research staffs were enlarged to include new specialists: Physicists and chemists analyzed semiconductors to determine their potential advantages and to furnish facts necessary for the actual manufacture of transistors for computers.

To describe semiconductors theoretically, the solid-state physicist explained that the electron gains energy from heat or light, and jumps "quantum-mechanically" into a conduction band, leaving a "positive hole." But in addition to the theoretical description, experimental preparation of semiconductors was required; and this demanded a different and complementary approach: the chemist's view of the chemical constituents, and their arrangement, in semiconductors. The physicist had to learn chemistry and the chemist had to learn physics, so that they could specify and prepare materials with the required number of excess "holes" or electrons. Figure 1 shows such a configuration, demonstrating the meaning of a "hole."

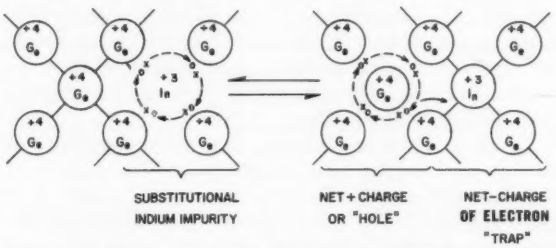


**Figure 1. Chemical configuration of a hole in germanium. When indium is substituted as an impurity into a germanium lattice site, only three covalent bonds are formed to the adjacent germanium atoms. The fourth germanium valence electron has no indium electron (indicated by dotted open circle) with which to pair, because indium has only three valence electrons (shown by open circles). The resulting electron lack "resonates" (as shown by dashed arrows) among all the germanium-indium bonds. When an electron migrates from an adjacent pure germanium site, all four germanium atoms are fully bonded to the indium atom, producing a net negative charge on the indium site and a net positive charge (hole) in the germanium lattice.**

As transistors have proved their value in computers, the increased study of semiconductors which resulted has firmly established the importance of chemistry, along with physics and quantum mechanics, in computer research. Physical chemists and X-ray crystallographers have been enlisted to study diffusion processes of micro-quantities of impurities in host semiconductor materials, and to grow and characterize crystals with such impurities to test the theoretical assumptions about them.

Transistors may have dramatized the emergence of chemistry as an active force in computer development, but semiconductor analysis is by no means the only assignment for chemistry in computer research. The current knowledge and methods of chemistry are also being applied to other materials and processes important to computer manufacturers. For example, photographic methods of handling data in computers are being considered and explored: Chemists are studying various photosensitive materials which might be incorporated successfully in data processing equipment for the entry, storage, and retrieval of information.

Data processing equipment could handle more information more rapidly if the computer memory units, where the information is stored, could be made more compact and more efficient. It has been known for some time that a photo-optical memory unit is theoretically possible, and that such a memory could surpass a magnetic unit in storage capacity. But present photo-optical memories are limited in that they are not reversible; tnat is, information cannot be changed once it is placed on the photosensitive medium.

Reversibility is not necessary in some applications, or is even undesirable; in such cases a non-reversible photosensitive material is acceptable and might be preferable. The translating machine developed at IBM, for example, stores an entire Russian dictionary, including idioms, in coded form on a 10-in. disk coated with a silver halide emulsion. In this application, where the information to be "remembered" by the unit is a long list, relatively permanent in content and arrangement, high-density storage is desirable for machine economy; non-erasability ensures the desired degree of permanence; and delayed processing is no particular disadvantage, since the list is seldom changed.

In other applications for a photosensitive memory unit, however, delayed processing may be a disadvantage. In connection with the problem of processing new entries to a memory unit during computer operation, we at IBM have recently studied the photoionization of a triphenylmethyl leuconitrile. This photochemical reaction has possible relevance because it produces color on irradiation alone, and thus might be a suitable medium for data storage in a computer. Our detailed study of the mechanism of this photochemical activity located certain controlling factors, and found some variations in the reaction: Under certain conditions, for example, fluorescence rather than photoionization takes place.

In the search for reversible photosensitive materials, another direction is being followed by the National Cash Register Company, whose chemists have developed the photosensitive spiropyrans shown in Figure 2—organic compounds which are bistable under irradiation by two different wavelengths of light. The usefulness of these compounds is limited by the fact that degradation products from the photochemical side reactions eventually interfere with reversibility; but in applications where only a few reversals are required, these compounds may be ideal.

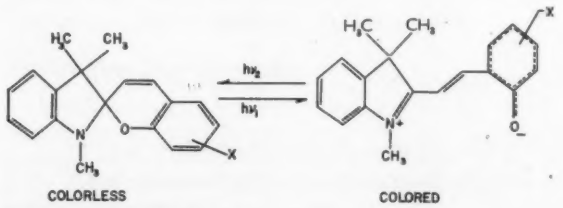


Figure 2. Spiropyrans.

Experiments reported at General Electric suggest that thermoplastic tape, which works on the simple principle of electrostatic attraction, might provide a reversible medium for data storage in computers. Their chemists prepared tape from a thermoplastic polymer such as polystyrene, charged selected areas of the tape with electrons from an electron beam, and then heated the tape. They found that electrostatic forces cause the material to deform under surface tension forces, leaving an erasable record of the electron beam.

These examples of current activity may seem to suggest that the chemist's present goal is to produce materials which could replace magnetic materials. If this were the only goal, the effort would be wasted. Rather we are examining broadly the several ways in which electromagnetic radiation affects materials. Magnetic fields interacting with ferromagnetic materials represent only one possible type of interaction. The study of the interaction of light with matter has already been mentioned to show that potentially useful processes may develop from this kind of basic investigation. It is true that the photosensitive materials developed so far cannot match all the capabilities of magnetic materials. They cannot be reversed as often or as rapidly; but they have other properties that magnetic materials do not possess. For example, photosensitive materials can store not only digital information but also photographic information; and there are numerous applications in which this ability would be useful.

Each material has its own unique advantages and disadvantages; it is necessary for the chemist to investigate these interactions to uncover all the significant variations. This area is one where physics and chemistry overlap strongly, and this fact again points up the need for inter-science cooperation.

Chemical research is attacking other problems: If we want to make smaller holes in accounting cards, we must understand the problems of dimensional stability of paper under varying conditions of humidity. If we want to specify a good magnetic ink, we must understand colloidal suspensions. If we want to make thinner and more uniform magnetic coatings on drums and disks, we must understand the mechanism of electroplating and the interaction of a pigment with its binder. If we want computers which are more sophisticated and more compact, we must—as we have seen—understand and exploit the processes of matter at the molecular level, which is also the province of chemistry.

Here again, as in our earlier examples, the chemist must work closely with other scientists. This interdependence is by no means unique to chemistry or to computer technology. Wherever the fundamental nature and processes of matter are being studied (and in this atomic age they are being studied everywhere), the old distinctions of separate sciences and separate science buildings on college campuses are now unrealistic. It is to be hoped that before long the traditional departmental division between physics and chemistry, for instance, will be abandoned in our universities. I believe this change should be recommended now on the graduate level. The terms "physical chemistry" and "chemical physics" are not semantic innovations; they are designations necessitated by the emerging facts. The facts, and the interdependence they reveal, are not new: The new element is our recognition of how important they are to our future.

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*Report of the* New England Association of Chemistry Teachers

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# Redox Revisited

Teaching oxidation-reduction may develop a great deal of unnecessary confusion in the minds of students if clear distinctions are not made between the concepts of *stoichiometry* and *mechanism*, as well as between *valence* and *oxidation state*.

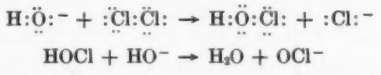
The methods taught for balancing oxidation-reduction equations involve the moving of electrons, the use of certain ions or radicals whose identity may be in doubt, or the introduction of artificial devices (such as the participation of water as hydrogen or hydroxyl ions).[1] While these many methods may not be harmful for the student to learn, he soon gets the notion that the actual reactions follow the paths that he is writing on paper; in other words, he develops the idea that he is dealing with the actual mechanism of a reaction when, in fact, he is merely balancing most oxidation-reduction equations stoichiometrically. Stoichiometric equations are important for making calculations involving the weight relations, and the stoichiometric equation must represent the correct net result of all the steps (partial reactions) in the reaction. The mechanisms of the steps may or may not be known, or the steps themselves may not even be fully identified, but the stoichiometric equation does not ordinarily convey the implication of mechanism.

Students should be told clearly what they are learning in the initial stages of balancing equations. They should be told that in some instances the oxidation-reduction equations do tell the correct story about mechanism, but that in many cases, these equations do not. Perhaps some clear pictures of mechanisms of certain simple reactions should be given at the same time the mechanics of balancing equations is introduced. The following examples are given to illustrate this point.[2]

The reaction of the halogens with base is represented as a redox reaction, and it is frequently shown only as

$$2\ NaOH + Cl_2 \rightarrow NaOCl + NaCl$$

If the reaction is examined in detail, it may be seen to involve (at least) two steps, a nucleophilic attack by the hydroxyl ion on a chlorine molecule, followed by a simple acid-base reaction:



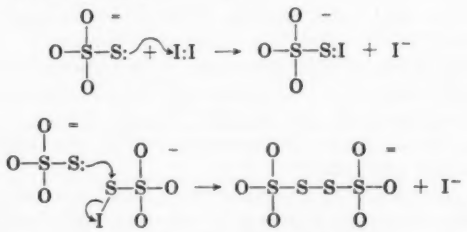
$$HOCl + HO^- \rightarrow H_2O + OCl^-$$

Such a presentation might provide a means of introducing such terms as "nucleophilic," "spectator ions," relative acid-base strengths, and so on.

The widely used reaction of thiosulfate with iodine is stoichiometrically balanced as follows:

$$2\ Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\ NaI$$

From the mechanistic standpoint, it is more complicated in that it involves several displacements:



Tetrathionate

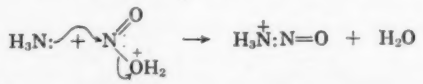
The simplicity of the stoichiometrically balanced equation for the formation of nitrogen and water by the decomposition of ammonium nitrite belies its actual complexity:

$$NH_4NO_2 \rightarrow N_2 + 2\ H_2O$$

Its actual mechanism may involve the following path; it leads nicely into the mechanisms of organic diazotization reactions:

$$NH_4^+ + {}^-O{-}N{=}O \rightarrow NH_3 + HONO$$

$$NH_4^+ + HONO \rightarrow H_2{}^+ONO + NH_3$$



$$H_3N{-}N{=}O + H_2O \rightarrow H_2N{-}N{=}O + H_3O^+$$

$$H_2N{-}N{=}O \leftrightharpoons HN{=}N{-}OH \text{ (Tautomeric Shift)}$$

$$H_3O^+ + HN{=}N{-}OH \rightarrow H_2O + HN{=}N{-}\overset{+}{O}H_2$$

$$H{-}N{=}N{-}\overset{+}{O}H_2 \rightarrow H_3O^+ + N{\equiv}N$$

It is recommended that the teaching be carried one step further, to the point of saying that balancing these complex equations, by whatever is the chosen method in the hands of the teacher, is purely an algebraic process, and that one method is as good as another. Perhaps several methods ought to be taught to the student

[1] Current thinking on these methods has been summarized and criticized in these recent articles: BURRELL, H. P. C., J. CHEM. EDUC., **36**, 77 (1959); YALMAN, R. G., J. CHEM. EDUC., **36**, 215 (1959); and PERKINS, A. J., J. CHEM. EDUC., **36**, 474 (1959).

[2] GOULD, EDWIN S., "Inorganic Reactions and Structure," Henry Holt and Co., Inc., New York, 1955. The examples cited are from pages 211, 210, and 240, in that order. Others may be found throughout the text.

to encourage him to think his own way through several, thus to see that the process is purely a mechanical one. Ultimately, he should be encouraged to choose that method which seems shortest and most efficient to him.

To avoid the confusion between stoichiometry and mechanism, an attempt has been made to teach the balancing of equations by a purely artificial method, carried to the furthest extreme. The concept of "oxidation state" or "oxidation number" has been exploited for this, and all reference to the gain or loss of *electrons* is avoided. The method has a great deal of similarity to the so-called "valence-change" method, because this seems to be among the shortest of the conventional methods. *Oxidation* is defined simply as an increase in oxidation state or a gain in positive oxidation number. *Reduction* is a decrease in oxidation state or a loss in positive oxidation number. This seems to avoid the frequently confusing notion that oxidation is a *loss* of electrons but an *increase* in oxidation state.

In the use of this method, a great deal of effort is made to make a distinction between "valence" and "oxidation state." Valence is defined as the total number of bonds which an atom, ion, or group demonstrates to other atoms, ions, or groups, in a compound. It is a number arrived at simply by counting bonds, and it is intimately related to structure. It is the classical "combining power" of an atom and, in contrast to oxidation number or state, has the greater physical reality; and it really is "combining capacity" since valence has nothing to do with "power."

Oxidation number or state is simply the number obtained when a set of arbitrary rules is applied to a given situation. The principal use of the oxidation number, aside from the classification of reactions as to type, is in the balancing of equations and, as long as the rules are followed, a stoichiometrically balanced equation results. A teacher should not be reluctant to calculate the oxidation number of Fe in $Fe_3O_4$ as $2^2/_3$, or of S in $Na_2S_4O_6$ as being $2^1/_2$. These strange values for the oxidation number arise simply because the value is an average value per atom and does not account for structural differences between two or more like atoms in a given compound. A good example to illustrate this is ammonium nitrate. If the formula of the compound is written $NH_4NO_3$, it can be easily seen that the oxidation number of the ammonium nitrogen is $-3$, while that of the nitrate nitrogen atom is $+5$. However, writing the formula of the compound $N_2H_4O_3$ leads to the average value for the oxidation number of each nitrogen $+1$.

### Establishing Oxidation States

A rather complex system of rules is proposed for the calculation of oxidation states. The list is not as formidable as it may seem initially, because not all the rules are used continuously, and many are based on previous knowledge.

1. The algebraic sum of the oxidation states of all the atoms in a neutral compound must equal zero, or it must equal the electrical charge on an individual ion.
2. The oxidation state of all elements in the free state is zero.
3. When an atom is bonded to an atom identical to it, this bond makes no contribution to the oxidation state of either atom.
4. The oxidation state of the elements of Group I of the Periodic Table is $+1$ in compounds, and the oxidation state of the elements of Group II is $+2$.
5. The oxidation state of oxygen is $-2$. Note that oxygen in peroxides has an oxidation number of $-1$, by application of rule 4.
6. The oxidation state of hydrogen is $+1$ in all its compounds except the hydrides, in which it is $-1$.
7. In those cases where the above rules cannot be applied directly or indirectly, the oxidation state of one element with respect to another on a given bond is determined from the relative electronegativities of the two elements in question. This rule becomes applicable frequently with such atoms as S and N in complex organic molecules.

***Examples:***

(The oxidation number of the italicized atom is given in parentheses after the compound) $H\mathit{Cl}O_3$ $(+5)$; $K\mathit{Mn}O_4$ $(+7)$; $\mathit{C}H_4$ $(-4)$; $\mathit{C}H_3OH$ $(-2)$; $H\mathit{C}HO$ $(0)$; $\mathit{C}O_2$ $(+4)$; $CH_3\mathit{C}OCH_3$ $(+2)$; $\mathit{C}H_3SO_3H$ ($-2$ for carbon, $+4$ for sulfur); $Na_2\mathit{S}_2O_3$ $(+2$, the average value for each S atom).

*Hydrocarbons* (where R is attached through a C—C bond): $R\mathit{C}H_3$ $(-3)$; $R_2\mathit{C}H_2$ $(-2)$; $R_3\mathit{C}H$ $(-1)$; each carbon atom of benzene $(-1)$.

*Derivatives* where "X" is F, Cl, Br, I, OH, O-alkyl, $NH_2$, SH, $NO_2$, etc.: $R\mathit{C}H_2X$ $(-1)$; $R_2\mathit{C}HX$ $(0)$; $R_3\mathit{C}X$ $(+1)$.

*Olefins:* $=\mathit{C}H_2$, terminal $(-2)$; $=\mathit{C}HR$ $(-1)$; $=\mathit{C}R_2$ $(0)$.

*Acetylenes:* $\equiv\mathit{C}H$ $(-1)$; $\equiv\mathit{C}R$ $(0)$.

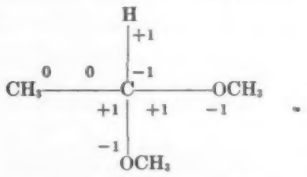
*Carbonyl compounds:* $R\mathit{C}HO$ $(+1)$; $R_2\mathit{C}O$ $(+2)$.

*Derivatives* where "X" is F, Cl, Br, I, OH, $NH_2$, SH, O-alkyl; $R\mathit{C}OX$ $(+3)$.

*Nitriles:* R—$\mathit{C}\equiv$N $(+3)$.

Where structure is known, one atom may be singled out of a large molecule for calculation of its oxidation state. In such cases, it is often convenient to think of the contribution of each atom to the oxidation state of the polyvalent atom in question. In covalent compounds these contributions depend on differences in electronegativities (rule 7).

For example, to determine the oxidation state of the italicized carbon in $CH_3\mathit{C}H(OCH_3)_2$, it is convenient to consider the pairs of atoms connected to each of the four bonds on this carbon. The contributions of the four atoms to the carbon in question are fixed by the rules or by differences in electronegativities:




The contribution of the $CH_3$—C bond is fixed by rule 3; that of the H—C bond, by rule 6; and that of the two $CH_3O$—C bonds by rule 7. The net oxidation state of the carbon atom is simply the sum of its "responses" to the oxidation states of its four attached groups, $+1$.

No attempt should be made to assign valences to any of these atoms apart from structural considerations. In all the compounds in the list containing carbon, for example, the valence of the carbon atoms is 4 (not $+$ or $-$) in spite of the spread in oxidation numbers from $+4$ to $-4$.

An important consequence of these concepts and the use of such a set of rules is that an oxidation number (except those elements in Groups I & II) has no significance apart from some specifically identified compound. For example, it is meaningless to say that the oxidation number of sulfur is $-2$, unless reference is made specifically to the sulfides. This is also true of the concept of valence.

## Balancing Redox Equations

The following steps are suggested for balancing oxidation-reduction equations:

(1) Write the equation showing all the reactants and the products.
(2) Find the atoms which change oxidation number.
(3) Balance the coefficients of the atoms identified in step (2).
(4) Do not subsequently change any of these coefficients obtained from balancing the oxidation-reduction involved in the reaction.
(5) Start with the metals at the left and balance their coefficients.
(6) Balance the coefficients of the non-metallic groups which go through the reaction unchanged.
(7) Balance the hydrogen next.
(8) There should be nothing left except oxygen. The oxygen must balance at this point if everything else balances, and this step should serve as a check on the work. If the oxygen does balance, the equation is correct.

***Examples*[3]:**

(1) $KMnO_4 + HCl \rightarrow MnCl_2 + Cl_2 + KCl + H_2O$
(2) The Mn is reduced ($+7 \rightarrow +2$) the Cl is oxidized ($-1 \rightarrow 0$)
(3) Since two HCl must always be required to form $Cl_2$, insert the necessary coefficient immediately, then calculate the changes in oxidation numbers.

2 (−1) to 2 (0) = gain of 2 units

$$\underset{+7}{KMnO_4} + 2\,HCl \rightarrow \underset{+2}{MnCl_2} + Cl_2 + KCl + H_2O$$

loss of 5 units

The number of oxidation units lost must equal the number gained.

10 (−1) to 10 (0) = 10 units gained

$$2\,KMnO_4 + 10\,HCl \rightarrow 2\,MnCl_2 + 5\,Cl_2 + KCl + H_2O$$

2 (+7) to 2 (+2) = 10 units lost.

(5) Balance K and Mn.

$$2KMnO_4 + 10\,HCl \rightarrow 2MnCl_2 + 5Cl_2 + 2KCl + H_2O$$

(6) It is now apparent that 6 additional chloride ions are required. Since these are not necessary for the oxidation reduction involved, they are sometimes referred to as "spectator ions."
(7) $2\,KMnO_4 + 16\,HCl \rightarrow 2\,MnCl_2 + 5\,Cl_2 + KCl + 8\,H_2O$
(8) Finally, it is seen that the oxygen checks.

The next example is given to show how it is possible to avoid the use of fractional oxidation states, if this is considered to be desirable.

(1) $K_2Cr_2O_7 + Fe_3O_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$
(2) Treat the "$Fe_3$" and the "$Fe_2$" as groups. Two $Fe_3$ groups in a "group oxidation state" of +8 are oxidized to 3 $Fe_2$ groups in an oxidation state of +6. (The same result is achieved if each Fe is considered to be oxidized from oxidation state of $+2\frac{2}{3}$ to +3). Each Cr is reduced, $+6 \rightarrow +3$; or, each $Cr_2$, $+12 \rightarrow +6$.

2 (+8) to 3 (+6) = gain of 2 units

$$K_2Cr_2O_7 + 2\,Fe_3O_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

+12 to +6 = loss of 6 units.

[3] For simplicity, the ionic condition of species will be assumed, e.g., KCl must not be thought of as a molecule, but as $K^+$ ion paired for stoichlometric convenience with a $Cl^-$ ion.

(3) By cross-multiplication (note that cross-multiplying by 6 and 2 followed by factoring gives the same result as multiplying by 3 and 1):

6 units gained

$$K_2Cr_2O_7 + 6\,Fe_3O_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 9\,Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

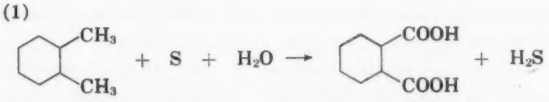
6 units lost

(5) Only K remains to be balanced, since step (4) is in effect:

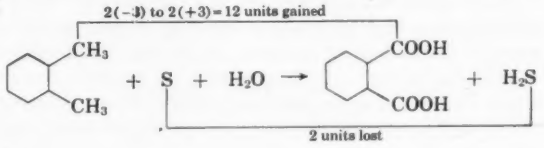
(6,7) $K_2Cr_2O_7 + 6\,Fe_3O_4 + 31\,H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 9\,Fe_2(SO_4)_3 + K_2SO_4 + 31\,H_2O$

A recently disclosed equation for the industrial preparation of phthalic acid may be balanced in this same fashion.

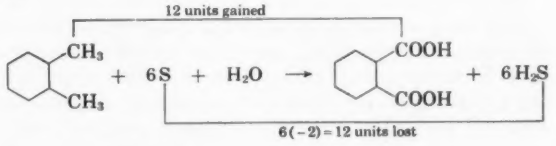
(1)



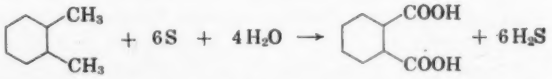
(2) Sulfur is reduced ($0 \rightarrow -2$). Each carbon atom of the methyl groups of the xylene is oxidized ($-3 \rightarrow +3$).




(3)



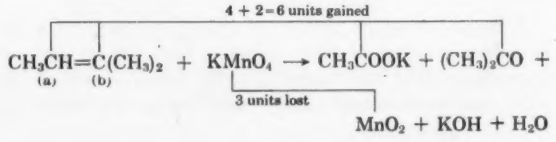

Step 5 does not apply.
(6) Through application of step (4), the H can be balanced only by adjusting the coefficient of the water:



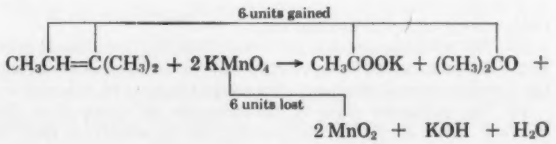
(7) The oxygen is seen to be balanced.

An example for an organic oxidation:

(1) $CH_3\underset{(a)}{C}H{=}\underset{(b)}{C}(CH_3)_2 + KMnO_4 \rightarrow CH_3COOK + (CH_3)_2CO + MnO_2 + KOH + H_2O$
(2) The Mn of $KMnO_4$ is reduced, $+7 \rightarrow +4$. Carbon atom (a) is oxidized, $-1 \rightarrow +3$ in $CH_3COOK$. Carbon atom (b) is oxidized $0 \rightarrow +2$ in acetone.




(3)



(4,5,6) No hydrogen is available for the formation of water.

$$CH_3CH{=}C(CH_3)_2 + 2\,KMnO_4 \rightarrow CH_3COOK + (CH_3)_2CO + 2\,MnO_2 + KOH$$

(7) The oxygen is seen to be balanced.

### Equivalent Weights

The definition of "equivalent weight" is pertinent here. At the risk of ignoring the historical implications of this term, it is proposed to define *equivalent weight* of an oxidizing or reducing agent as simply the formula weight divided by the number of oxidation units lost or gained by some atom in the oxidizing or reducing agent, respectively. This may have little to recommend it besides pragmatic value in the laboratory, since it is deliberately devoid of theoretical implication.

In the above examples, the fractions of the formula weights which are the equivalent weights are in the table:

Table 1

| Equivalent weight oxidizing agent | | Equivalent weight reducing agent | |
|---|---|---|---|
| $KMnO_4$ | $^1/_5$ | HCl | 1 |
| $K_2Cr_2O_7$ | $^1/_6$ | $Fe_3O_4$ | 1 |
| S | $^1/_2$ | Xylene | $^1/_{12}$ |
| $KMnO_4$ | $^1/_3$ | $CH_3CH{=}C(CH_3)_2$ | $^1/_6$ |

It should be emphasized that it is impossible to calculate equivalent weights without knowing the reaction.

Chem Ed

# LETTERS

*To the Editor:*

The article of Nyburg and Halliwell, "A Geometric Approach to Extensive Properties," appearing in the March issue [**38,** 123 (1961)] is very interesting and enlightening and they are to be complimented upon it.

It appears to this reader that the $(\partial X/\partial n_1)_{n2}$ and $(\partial X/\partial n_2)_{n1}$ terms on page 125 of the article should be transposed. Figure 8 then becomes merely the $n_1 + n_2 = 1$ cross-section of Figure 7, in which $n_1 = x_1$, the mole fraction of component 1 (varying from 0 at $G'$ to 1 at $H'$) and $n_2 = x_2$, the mole fraction of component 2 (varying from 0 at $H'$ to 1 at $G'$). In Figure 8, $x_1$ and $x_2$ should then be transposed and $A$, $B$, $F$, and $E$ may be replaced by $H'$, $B'$, $D'$, and $G'$, respectively. Then, by the reasoning given,

$$\bar{X}_1 = (\partial X/\partial n_1)_{n2} = B'H',$$
$$\bar{X}_2 = (\partial X/\partial n_2)_{n1} = D'G',$$

and

$$\left(\frac{\partial X}{\partial x_1}\right)_{n1\,+\,n2} = 1 = \frac{X - \bar{X}_2}{x_1} = \frac{\bar{X}_1 - \bar{X}_2}{1} = \left(\frac{\partial X}{\partial n_1}\right)_{n2} - \left(\frac{\partial X}{\partial n_2}\right)_{n1}$$

$X$ may then be obtained as described in the article or by evaluating the integral

$$\int_{\bar{X}_2}^{X} dX = \int_0^{x_1} \bar{X}_1 dx_1 - \int_0^{x_1} \bar{X}_2 dx_1$$

DWIGHT F. MOWERY, JR.

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NEW BEDFORD, MASSACHUSETTS

EDITOR'S NOTE: The Editor and the authors regret not spotting this inconsistency before publication. Readers also may note that one can also transpose $x_1$ and $x_2$ in Figure 8 to match Figure 7 more closely, but the derivation in the text must be altered accordingly.

*To the Editor:*

Following the recent description in THIS JOURNAL [**38,** 29 (1961)] by Stearns and Mucci of the use of $Ba^{137m}$ to determine the resolving time of a G-M counter, your readers may be interested in an alternative separation of this nuclide from its parent, $Cs^{137}$, which has been in use at this College over the past three years. Cesium is strongly and selectively retained in acid solution by a pre-formed precipitate of ammonium 12-molybdophosphate (AMP). This enables a "barium cow" to be set up as follows:

AMP is prepared by adding 1 ml of concentrated nitric acid and 0.5 g of ammonium nitrate in approximately 7 ml of distilled water to a solution containing 6 mg of phosphate ion, as ammonium dihydrogen orthophosphate. A 3 ml portion of 10% ammonium molybdate solution is then added, and the mixture placed in a water bath at 80°C for 20 minutes. The precipitate is separated under slightly reduced pressure, on a Whatman No. 1 filter-paper in a 1-in. diameter demountable Buchner funnel and washed with distilled water. Care is taken to ensure that the AMP (approximately 120 mg) is distributed evenly over the filter paper. Approximately 10 ml of a solution of $Cs^{137}$ in 2 $M$ nitric acid is then allowed to flow through the bed of AMP; cesium is retained while $Ba^{137m}$ remains in solution. After allowing a few minutes for growth, a further supply of $Ba^{137m}$ may be washed out with 2 $M$ nitric acid, and assayed with a liquid Geiger counter.

Such a barium cow will, if kept moist, give a supply of $Ba^{137m}$ over many months. We normally use this nuclide as an alternative to protactinium-234 to provide a demonstration or student experiment on the determination of a comparatively short half life. The bed of cesium-loaded AMP, immediately after washing with acid, may be transferred complete with funnel to an end-window type of counter for observation of the growth curve of $Ba^{137m}$ in its parent; a *gamma*-scintillation counter is best for this purpose, as it avoids counting the *beta* particles of $Cs^{137}$.

R. W. C. BROADBANK
and R. D. HARDING

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LEICESTER, ENGLAND

Chem Ed

# BOOK REVIEWS

### Synthetic Methods of Organic Chemistry. Volume 14

*W. Theilheimer.* S. Karger, Interscience Publishers, Inc., New York, 1960. xvi + 549 pp. Many figures. 16.5 × 23.5 cm. $29.50.

In this handy book the author again succeeds in providing an annual handy reference for "new methods of synthesis of organic compounds, improvements of known methods, and also old proved methods scattered in periodicals." In the present volume there are 995 monographs, over 453 pages of texts. There follow 95 pages of indices which not only index the material in the present text but also cross reference to pertinent items in previously published volumes of the series. The monographs are indexed uniquely, according to a simple system created by the author (see Vol. 2).

Again in this volume, the section on trends in synthesis which precedes the pages of monographs, is an interesting and informative section. Some of the examples cited at random from this section are the use of triarylalkyl borons for the preparation of other organometallic compounds, for example, for dialkylmercury even in aqueous solution, a new aldehyde synthesis from acid derivatives through 1-acylpyrazoles, the selective cleavage of esters with lithium iodide, a new and simple technique for the replacement of diazonium by nitro groups which gives high yields in certain cases, and the use of dimethyl sulfoxide as an excellent solvent for the conversion of alkyl chlorides into the corresponding nitriles.

Many examples could be chosen from the text to illustrate the author's awareness of and sensitivity to new techniques as published in the literature. Some of these are the use of ruthenium tetroxide as a powerful oxidizer, the oxidation of methyl groups with sulfur and sodium hydroxide, the introduction of trifluoromethyl groups into heterocyclic compounds and a modification of the Guerbet condensation, using potassium hydroxide and boron anhydride.

As the reviewer recommended in his prior review (THIS JOURNAL **37,** 218 (1960)), practicing organic chemists will find browsing through this text a rewarding experience; the book is highly recommended for this purpose.

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*Brooklyn, New York*

### Isotope Effects on Reaction Rates

*Lars Melander,* Nobel Institute of Chemistry, Stockholm, Sweden. The Ronald Press Co., New York, 1960. vi + 181 pp. Figs. and tables. 14 × 21 cm. $6.

Following a brief introductory chapter which includes some general references to the subject of isotope effects, the topics of Chapters 2 through 9 are as follows: Prediction of Rate-Constant Ratios from Molecular Data; Evaluation of Rate-Constant Ratios from Experimental Data; Primary Hydrogen Isotope Effect in Single Reaction Steps; Secondary Hydrogen Isotope Effects; Hydrogen Isotope Effects and Reaction Mechanisms; Carbon Isotope Effects in Single Reaction Steps; Carbon Isotope Effects and Reaction Mechanism, and finally, Isotope Effects with Elements Heavier than Carbon.

Chapter 2 is by far the most important in the book, for Melander starts with the theory of absolute reaction rates, and discusses the physical meaning of each mathematical component of the relationships which comprise the present day isotope effect theory. The development is done in a straightforward, almost conversational, fashion, and one need not follow the mathematics closely to understand the principles involved. The simplifying assumptions which are necessary in modifying the "primary relationship" and the "complete" equation of Bigeleisen so that they might be applied in specific instances are presented and discussed. On page 42 a chart is given which interrelates the different expressions and approximations in a descending scale of utility from heavy isotopes to isotopic hydrogen. Both the strength and the weaknesses of the theory are impartially presented in a proper perspective.

In Chapter 3 Melander discusses and illustrates, with appropriate plots, both the cumulative and differential relationships between isotopic ratios of reactant and product as functions of fraction of reaction and isotope effect. The concept of the "lagging" of the heavier isotope is a much misunderstood factor, and yet a clear knowledge of it is essential to a proper evaluation of tracer results. Chapter 3 should, therefore, be of great importance to organic chemists and to biochemists who work with the isotopes of carbon and hydrogen.

The remainder of the book is devoted to discussions of specific examples of primary and secondary hydrogen isotope effects, to effects with carbon, oxygen and sulfur, with special emphasis upon what type of mechanistic information can be gleaned from such studies.

In the Preface, Melander admits the subjectivity with which he chose certain references for discussion. Such is always an author's privilege however, and by having placed his stress upon principles rather than upon a comprehensive treatment of the literature of isotope effects, the author has imparted readability and simplicity to his book.

This is an outstanding, well-written book about a very important field of science. It is also authoritative, for there are, beside Melander, perhaps only one or two others with sufficient firsthand knowledge to have written it. It should appeal to the beginner and expert alike and should be on the desk of every research scientist who uses isotopes.

CLAIR J. COLLINS
*Oak Ridge National Laboratory*
*Oak Ridge, Tennessee*

### Theory of Detonation

*Ia. B. Zeldovich* and *A. S. Kompaneets.* Academic Press, Inc., New York, 1960. 284 pp. Figs. and tables. 16 × 23.5 cm. $10.

This is a recent publication in translation of a book which was first published in Moscow in 1955. The book is based on

**Reviewed in This Issue**

*W. Theilheimer,* Synthetic Methods of Organic Chemistry. Volume 14
*Lars Melander,* Isotope Effects on Reaction Rates
*Ia. B. Zeldovich* and *A. S. Kompaneets,* Theory of Detonation
*Paul Pascal,* Editor, Nouveau Traite de Chimie Minerale. Volume 15
*Frederick L. Fitzpatrick,* Editor, Policies for Science Education
*R. B. Heslop* and *P. L. Robinson,* Inorganic Chemistry: A Guide to Advanced Study
*M. Stacey* and *S. A. Barker,* Polysaccharides of Micro-Organisms
*Adrien Albert,* Selective Toxicity
*John T. Edsall,* Editor, Amino Acids, Protein, and Cancer Biochemistry
*R. M. Acheson,* An Introduction to the Chemistry of Heterocyclic Compounds
*E. H. B. Pietsch,* Editor, Gmelins Handbuch der Anorganischen Chemie. 8 Auflage. System Nummer 15, Silicium, Teil B
*Van R. Potter,* Nucleic Acid Outlines. Volume 1
*C. K. Ingold,* Substitution at Elements other than Carbon
*Ralph T. Overman* and *Herbert M. Clark,* Radioisotope Techniques.
*Ralph A. Raphael, E. C. Taylor,* and *Hans Wynberg,* Advances in Organic Chemistry: Methods and Results. Volumes 1 and 2
*Louis F. Fieser* and *Mary Fieser,* Style Guide for Chemists.
*Marcel Florkin* and *Howard S. Mason,* Comparative Biochemistry. Volume 1, Sources of Free Energy
*Melvin S. Newman,* Editor, Organic Syntheses. Volume 40

papers of the Chemical Physics Institute of the Academy of Sciences of the USSR pertaining to the hydrodynamics of flames and detonation waves.

The first chapter of the book deals with the elements of gas dynamics as applied to strong and weak shock waves. The second part deals with detonations and lossless combustion in which there is energy release from chemical reaction to support the propagation of the wave. The propagation of flames under varying boundary conditions such as in open and closed end pipes, and stationary combustion in a flow system are discussed.

The third part of the book discusses boundary losses and the effects of friction and heat transfer on the propagation of detonation waves. Chapter Four takes up the topic of detonations in condensed explosives and describes some attempts to work towards the experimental data with simple models.

The Fifth and final chapter of the book deals with motion of detonation products in the rarifaction waves which follow the reaction zone. The problem is discussed in one and two dimensions and for the spherical case.

This book is a valuable contribution as a key to the Russian literature on combustion hydrodynamics which is too frequently overlooked. Fewer than six references are given to non-Russian work, so the book is less than a general reference. The relatively early first publication date prevented any inclusion of much recent work. For these reasons there is no reference to the experimental work of Kistiakowsky or that of the workers at Los Alamos. The theoretical papers of Kirkwood and their implications are not included, and the contributions of von Neumann and Doering are absent. The book is concerned almost entirely with hydrodynamics, and there is none of the recent work cited dealing with chemical species, chemical kinetics and energy transfer in combustion phenomena.

The specialist in gas dynamics and combustion will be interested in this book, but the general reader will probably be more satisfied with a coverage such as is found in Lewis and von Elbe, "Combustion Flames, and Explosions of Gases."

JOHN P. CHESICK
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*New Haven, Connecticut*

### Nouveau Traitè de Chimie Minèrale. Volume 15

Edited by *Paul Pascal*, Sorbonne, France. Masson et Cie, Paris, 1960. xix + 734 pp. Figs. and tables. 18 × 26 cm. Broché 115 NF, Cartonné toile 127 NF.

The fifteenth volume of Pascal's new treatise deals with uranium and the transuranium elements. It will appear in two sections, with the first devoted to uranium and the second to the transuranium elements. The volume is being published with the collaboration of the French Commissariat for Atomic Energy.

Included in the general bibliography is a list of abbreviations of laboratories of the United States, Canada, Great Britain, France, and Italy from which atomic energy research reports originated. The general introduction is by M. Salesse, Chief of the Department of Metallurgy of the Commissariat for Atomic Energy, and the greatest emphasis is placed upon the aspect of radioactivity and atomic energy. The work has been written by many, rather than a few, authors.

It is recognized that uranium is so intimately connected with atomic energy that much emphasis must be placed upon it in any treatise which deals with the element, but it is felt that this section of the volume has placed much more emphasis on piles, reactors, and atomic and nuclear energy than necessary on a work which should be concerned with the element uranium as such. These parts appear to have been written more for the engineer than for the theoretical and physical chemist.

This part of the volume is well illustrated and has reasonably up to date bibliographies. The parts devoted to isotopes and minerals of uranium are excellent.

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*Gainesville*

### Policies for Science Education

Edited by *Frederick L. Fitzpatrick*, Teachers College, Columbia University, New York. Bureau of Publications, Teachers College, Columbia University, New York, 1960. xiii + 219 pp. $3.95.

This volume is one of a series of monographs produced by The Science Manpower Project. The monographs already published have dealt, in general, with specific courses in science and with the people who may be students in them. The present volume attempts to accomplish a most laudable goal—that of pointing the way to the formulation of a much-needed statement of general policy for the field.

The approach deals appropriately with such background factors as the nature and extent of the need for scientists, engineers, and technicians, the expanding economy, the functions of science education, and the quantity and quality of those persons who teach science. Early in the volume the groundwork is neatly delineated for the solution of certain current problems: public support and understanding must be gained.

The writers of the volume ask a pertinent question: "Who *should* determine policies for science education?" Their answer is "science educators in schools and colleges should take the major responsibility." Many readers will not be certain of the identity of the "science educator" as the term is used here. Some who choose a limited definition will disagree; perhaps others with a broader definition will enthusiastically endorse the position.

After a survey of school administration, the work of science teachers, and public relations, the volume proceeds to an examination of science programs. In a general way curriculum and method are described with suggestions for improvement. Then the spotlight is placed on the science teacher—his background and his work. The preparation and certification of the teacher come under scrutiny. The concluding chapter proposes a school program in science that will take into account science manpower needs, general community factors, and general school factors. Certain outlines for programs for teacher preparation are provided. Finally, a summary composed of statements of principles, recommendations, beliefs, and facts is provided.

The monograph draws obviously upon a broad range of the experience of science teachers. In many places reference is made to facts and figures pertinent to the topic at hand. For readers well informed in the field of science education this contribution summarizes and integrates very well a functional philosophical position, the results of some research, and common knowledge of the field. Those less acquainted with the field will look for greater documentation than is provided in this report; but if such persons will read with care, they will surely come to agree with the science educator that perhaps the greatest need of science education today is fundamental research on such problems as how people learn, how science can be taught effectively, and how science teachers should be prepared.

JOHN S. RICHARDSON
*Ohio State University*
*Columbus*

### Inorganic Chemistry: A Guide to Advanced Study

*R. B. Heslop*, Manchester College of Science and Technology, and *P. L. Robinson*, Atomic Energy Research Establishment, Harwell, England. Elsevier Publishing Co., Amsterdam, 1960; sole distributors for the U.S., D. Van Nostrand Co., Inc., New York. viii + 555 pp. Figs. and tables. 16 × 23 cm. $9.

In the preface the authors state that "a point has been reached in the development of the subject (inorganic chemistry) from which it is easier and less confusing to enter it at the level of present theoretical and physical-chemical knowledge. This book attempts to provide such an entry." In this the authors partially succeed, although in the presentation of the descriptive chemistry of the elements a minimum of physical-chemical data are presented.

Like its predecessors, the book is essentially written in two parts. The first half covers the theoretical material in 10 chapters, and 206 pages, while the second part covers the descriptive chemistry of the elements in 26 chapters and 324 pages. After a brief introductory chapter, chapters on the Atomic Nucleus and Radiochemistry are introduced, followed by the chapter on the Electronic Structure of Atoms—The Periodic Table. This includes a brief mathematical description of the wave mechanical hydrogen atom,

the build up of the multielectron atoms, and a brief description of periodic properties. To this point the treatment of the material is more or less standard. In the next chapter on Valency the subject matter is dominated by the qualitative presentation of the molecular orbital approach to the chemical bond, with considerable emphasis on the hybrid nature of most covalent bonds. The description of electronegativity here is brief and does not consider the most recently refined data. The ligand field theory is introduced in the chapter on the Structure and Shape of Molecules. This chapter also includes two-paragraph thumbnail sketches of experimental techniques for structure determinations. In the next chapter on the Solid State the important structures are discussed, and a section on crystal growth is included. The theoretical section is concluded with chapters on Thermodynamics, Kinetics, and Acid-Base theory. The first two are very brief and essentially contain the elements of the theory rather than the practical application of the principles.

The descriptive chemistry section covers the whole periodic table. The elements are discussed in groups as defined by the long form of the periodic table, with separate chapters for hydrogen, the lanthanides, and the actinides. The nontransitional elements are discussed first, except for the inert gases, and Groups I and II are divided into two chapters for each group. Chapters on the transitional elements then follow. In general, the organization of these chapters follows a pattern, in which the electron configurations, radii, ionization potentials, electrode potentials, and the physical properties of the elements are presented in tables. The chemical properties of the elements and their preparation from a source material are then presented, followed by a discussion of the binary compounds such as the halides, oxides, and sulfides. Special type compounds associated with a particular group are usually taken up last in the chapter. The molecular orbital theory of bonding is used extensively in the discussion of the structural properties of the molecules. Electrode potentials are used in the discussion of the chemistry, but the use of other thermodynamic data is very limited.

Interspersed with the group chapters, are chapters on the Hydrides, Oxides, Halides, Coordination Compounds, and the Peroxides and Peroxocompounds. These chapters provide a very useful perspective not obtained from the group chapters.

In general, the book is up to date and accurate. There are some questionable statements or omissions, such as the lack of information on polymerized metal ion species in solution, the lack of structural data for $Mo(CN)_8^{-4}$, the acceptance of the still questionable resolution of $Fe(C_2O_4)^{-3}$, and comments on the nonexistence of $NbI_4$, and $M^{+4}$ ions in aqueous solution. Although a section is included on inorganic nomenclature of complex compounds, when such compounds are named we find reference to purpureo, luteo, and violeo. The Stock system of nomenclature is not used.

No general reference system is used, although if the authors felt that a particular discovery or concept was noteworthy, a date and name are included in the text in parentheses. There are no questions or practice exercises included.

This book is a welcome addition to the inorganic literature and will find wide acceptance because of its up-to-date application of molecular orbital theory to the chemical bond. The authors have a very readable style and have the ability to present complex concepts clearly with a minimum of words.

EDWIN M. LARSEN
*University of Wisconsin*
*Madison*

### Polysaccharides of Micro-Organisms

*M. Stacey* and *S. A. Barker*, both of the University of Birmingham, England. Oxford University Press, Inc., New York, 1960. ix + 228 pp. Figs. and tables. 15 × 22 cm. $4.80.

Polysaccharide chemistry is advancing rapidly over a broad front, quite unlike the slower progress which was being made only a few years ago. Then, advancement was largely associated with the better-known plant polysaccharides such as starch and cellulose, with the initiation of a formidable advance underway in the chemistry of hemicelluloses, seaweed polysaccharides and a few of the most abundant polysaccharides of animals and micro-organisms. Recently, with new and better techniques available, especially those in microchemistry, it has been possible to obtain concrete advances in the general chemistry and structure of the animal and microbial polysaccharides. Both of these groups of compounds are now under intensive investigation, and much information of a structural, general chemical and biological nature is appearing in the literature.

The present volume on the polysaccharides of micro-organisms is not a treatise and makes no attempt to present detailed information in this area. Rather, the purpose of the authors is to present a brief survey, summarizing the existing knowledge regarding the polysaccharides of Gram-positive and Gram-negative bacteria, viruses, rickettsia, moulds, yeasts, yeast-like fungi and protozoa. The first five chapters, covering 69 pages, describe briefly the occurrence of certain sugars and groups of sugars and microbial polysaccharides, and the function of polysaccharides, their isolation and the general approach to their structural determination. These brief chapters present a good survey of the subject area. Likewise, the remaining chapters present, in brief form, the salient developments in the chemistry and biochemistry of specific polysaccharides from micro-organisms. The reviewer likes the book and believes that it offers a good up-to-date survey of the subject. Continuation of the present rate of investigative advance will make it desirable and necessary to have periodic publications of this sort, by which persons interested in biology and macromolecular chemistry may quickly come abreast of this fascinating and significant field of research.

Nomenclature in the book is, on the whole, good. It is hoped that in the future the authors might work to extend preferred nomenclature. Especially, they should be encouraged to use the term aldobiouronic acid in place of the archaic aldobiuronic acid, because the modified disaccharides referred to have only one uronic acid group. Moreover, the term polyglucosan should be avoided since it signifies a polymer of an intramolecular anhydride. The term glucosan has now been well defined by the American and British Carbohydrate Nomenclature Committees. Polyglucosan, therefore, has at present no proper nomenclature significance in the polysaccharide field. Its place should be taken by the word glucan, which signifies a polysaccharide composed only of glucose units. It is also to be hoped that workers will not perpetuate the use of two different names for sugars which are mirror images. Thus, it is not desirable to use both the term abequose and the term colitose. The two sugars should either be called *D*- or *L*-abequose or they should be called *D*- or *L*-colitose.

The book is generally free of errors; however, on page 43 two basic resins are said to be in the "sodium form."

ROY L. WHISTLER
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### Selective Toxicity

*Adrien Albert*, Australian National University, Canberra, Australia. 2nd ed. John Wiley & Sons, Inc., New York, 1960. x + 233 pp. Figs. and tables. 14.5 × 22 cm. $5.50.

This is a much enlarged second edition of the stimulating work which first appeared in 1951. Chapters have been rewritten with the addition of pertinent new material. New topics have been treated.

The preface states that the first 4 chapters are suitable for undergraduate students and that the last 9 chapters are intended for the more advanced student. This book is not suitable for undergraduates and will prove frustrating at times to the more advanced student. This is disappointing to me since the concept of selective toxicity is well taken and is broadly examined.

Four main faults are the basis of this judgment. There are frequent ambiguities which would have been avoided by more careful writing. Many generic names are used without accompanying systematic names or structural formulae. References for key statements are frequently not present. Some general statements are not in accordance with published information.

Indefinite exposition is exemplified on page 7 where the rate of hydrolysis of tetraethylpyrophosphate is compared with those of certain unspecified "other" phosphate esters. The example of a Van der Waals' bond given in Table 1, page 85, is more conventionally restricted

(*Continued on page A426*)

# CHEMISTRY TEXTS FROM PRENTICE-HALL

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*by* WILLIAM L. JOLLY, *University of California, Berkeley*

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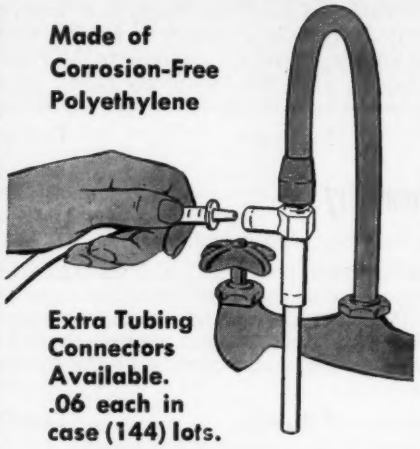

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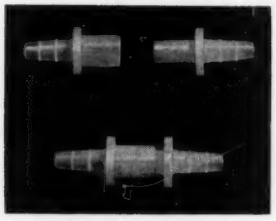

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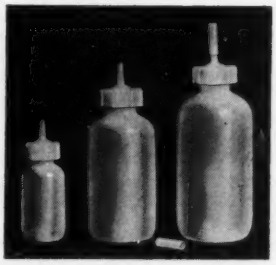

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# BOOK REVIEWS

to covalent bonds. The definition of a covalent bond on page 35 as "one which is not easily broken, e.g., by dissociation in water at 20°," does not include the C—Cl bond of acid chlorides and is not up to the general sophistication of the work. A better definition is to be found on page 86. The failure on page 73 to specify the species in discussing the mode of action of insecticides is another case of indefiniteness. The statement on page 80 that "growth inhibitory substances (does this include appetite depressants and distasteful materials?) are almost always carcinogenic" is unduly broad and without a reference. Indeed almost the entire section on carcinogenesis and the chemotherapy of cancer, pages 76–80, has unfortunate ambiguities and lack of references.

A particular example of the annoying use of generic or trivial nomenclature is on page 9. In one sentence six such names, of which only one has been defined, are used. On the same page, it would be more accurate to speak of diazinon(e) as being "a" rather than "the" pyrimidine analogue of parathion. Nomenclature confusion is also found on page 29 where it is implied that benemid and caronamid are the same compounds, and an ambiguous name is given. They are in fact different compounds.

Statements which are either too broad or not accurate can be found in several places. It is inaccurate to speak of the ready penetration of the blood brain barrier by sulfonamides (page 27), as there is considerable variation between the various derivatives of sulfanilamide. It is inaccurate that "bovine mastitis" . . . is now cured with "sulfanilamide" (page 8). The emergence of resistant species of bacteria have made the use of newer agents necessary for the control of this disease.

The statement on page 52 that $N^4$-methyl sulfanilamide is inactive *in vivo* is not correct as will be found by reference to E. H. Northey's "The Sulfonamides." It would be correct to state that metabolism undoubtedly removes the $N^4$-methyl group to give an active compound. Similarly, it is implied on page 98 that substituted sulfonamides are inactive as carbonic anhydrase inhibitors. This statement is true only *in vitro* as various alkyl groups can be metabolized *in vivo* to yield active compounds. The history of the discovery of the carbonic anhydrase inhibiting activity of sulfonamides is given inaccurately on page 97. It is to be traced to the observation that sulfanilamide causes an alkalinization of the urine of dogs, by E. K. Marshall (T. H. Maren, E. Mayer, and B. Wadsworth, Johns Hopkins Hosp. Bull., 95, 201(1954)) rather than to that given by Albert. Other examples of this sort could be cited.

Mechanical errors are few. It is to be regretted that the Dalmatian has been omitted from the footnote of Table 2 (page 16, First and Second Edition) in the Second Edition. On pages 78 and

*(Continued on page A428)*

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## COLLEGE CHEMISTRY: A Systematic Approach Second Edition

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## LABORATORY PRACTICE OF ORGANIC CHEMISTRY Third Edition

*by G. Ross Robertson, Professor Emeritus, University of California, Los Angeles*

The first half of this well-known manual contains an unusually detailed treatment of the principles underlying laboratory procedure in organic chemistry. Part Two includes not only directions for experiments, but also examples of qualitative analysis. Emphasis on theory is maintained throughout, and explanations of principles are kept distinct from directions for experiments.

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## PHYSICO CHEMICAL EXPERIMENTS

*by Robert Livingston, Professor and Chief of the Division of Physical Chemistry, University of Minnesota*

Experiments in this laboratory manual illustrate the basic principles and techniques of physical chemistry. Quantitative aspects of the work are stressed, and the student is given thorough training in computation. All procedures are clearly explained, but in some of the simpler experiments, only purpose and general methods are described, leaving the details of procedure for the student to work out as a minor research problem.

1957 273 pages $4.50

*The Macmillan Company*

60 FIFTH AVENUE, NEW YORK 11, N.Y.

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180, triethylenemelamine is incorrectly called tetraethylenemelamine and is incorrectly identified as TEPA. The citation of Roblin on page 103 does not appear in the bibliography.

If the reader can overcome these objections to the above criticized style, he will find Chapters 6 through 13 to be a useful review of the modes of action of various selectively toxic agents.

JACKSON P. ENGLISH
*American Cyanamid Company*
*Pearl River, New York*

**Amino Acids, Proteins, and Cancer Biochemistry**

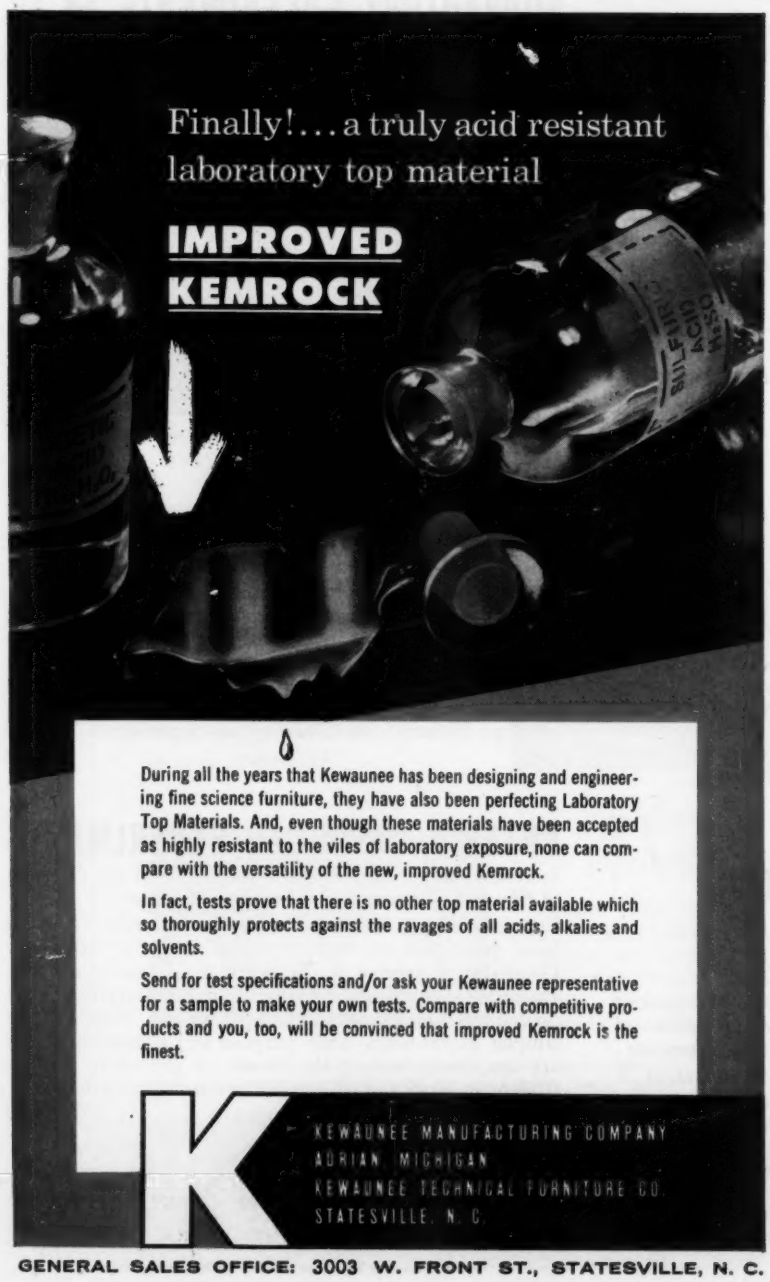
Edited by *John T. Edsall*, Harvard University, Cambridge, Massachusetts. Collection of papers presented by the Jesse P. Greenstein Memorial Symposium, Division of Biological Chemistry, ACS, September 16, 1959. Academic Press, Inc., New York, 1960. ix + 244 pp. Figs. and tables. 15.5 × 23.5 cm. $7.

The Memorial Symposium and *Festschrift* both afford unique opportunities for critical evaluation and speculation. Their very nature seems to eliminate the formality and sometimes labored detail of the typical review. The authors appear less constrained by the conventions of scientific writing and the discussions are free and interesting. "Amino Acids, Proteins, and Cancer Biochemistry," a memorial symposium in honor of Jesse P. Greenstein, is an important addition to this literature and a thoroughly interesting discussion of recent concepts and techniques in several areas of biochemistry. The articles form a coherent unit, perhaps because they review areas of biochemical research that were of importance in the investigations of one brilliant and versatile scientist. The introductory chapter, a critical tribute to Greenstein by Edsall and Meister, and the concluding section, a bibliography of Greenstein's published work, measure the breadth and competance of this man. The remainder of the symposium can be divided into two sections. The first section discusses techniques in amino acid and protein biochemistry while the second summarizes and evaluates concepts in intermediary metabolism which may be related to cancer biochemistry.

Winitz, Birnbaum, Sigimura, and Otey discuss the preparation of optically pure amino acids and their incorporation in water-soluble chemically defined diets. The application of these diets to problems in metabolism is a striking example of the information yet available in the so-called exhausted area of nutrition. Scheraga, Cha, Hermans, and Schildkraut discuss the internal hydrogen bonding in ribonuclease in a chapter as stimulating as the always interesting studies of Scheraga and his collaborators. Neurath, Rupley, and Vallee summarize the chemistry of metal free and native carboxypeptidase. These studies are especially interesting since they suggest that metal ions contribute to the formation of enzyme-substrate complexes. Sober and Peterson review their extensive contributions to the purification of proteins with cellulosic adsorbents. This chapter includes a number of examples of specific proteins and the partial enzymatic digest of RNA and is the more interesting since Kit discusses these techniques in his chapter on the characterization of nucleic acids in normal tissues and tumors.

The discussion of intermediary metabolism begins with a good critical review of amino acid activation and protein biosynthesis by Alton Meister. This chapter is followed by a discussion of Greenstein's generalization that the biochemical characteristics of tumors tend toward a common pattern. Weinhouse has written an interesting discussion of this generalization and a critical evaluation of Warburg's theory of impaired respiration in tumors. Roberts and Simonsen then summarize their very recent studies on free amino acids in normal and neoplastic tissue. Glutamine metabolism and the possibility of chemotherapeutic control of tumors through glutamine metabolism is an interesting aspect of this work. The chapter by Kit mentioned previously is a highly critical and necessary review of the characterization of nucleic acids. Racker, Wu, and Alpers then discuss carbohydrate metabolism, the Pasteur and

(*Continued on page A430*)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## INTRODUCTION TO CHEMICAL ENGINEERING

**By L. BRYCE ANDERSON, The Rice Institute; and L. A. WENZEL, Lehigh University.** *The McGraw-Hill Chemical Engineering Series.* **Available in June, 1961.**

Designed for a fast-paced, rigorous one semester course to introduce the sophomore to the chemical engineering profession and to the chemical process industries. The authors' objective is to cover the topics usually covered in stoichiometry, but also to give the student knowledge of and enthusiasm for the field of chemical engineering, so he will have a greater sense of purpose as he proceeds through subsequent courses.

## PRINCIPLES OF ORGANIC CHEMISTRY

**By JAMES ENGLISH and HAROLD CASSIDY, Yale University. Available in August, 1961.**

A general revision and updating of an established text intended primarily for full-year courses for ore-meds and other non-majors, but also suitable for one-semester courses. Avoiding the encyclopedic approach of some texts, the authors have been highly selective and present only those topics necessary to demonstrate basic principles.

## THERMODYNAMICS, Second Edition

**By B. N. LEWIS and M. RANDALL (Revised by KENNETH S. PITZER and LEO BREWER, both of the University of California, Berkeley).** *McGraw-Hill Series in Advanced Chemistry.* **723 pages. $12.50.**

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## THERMAL REGIMES OF COMBUSTION

**By L. A. VULIS: translated from the Russian by GLENN WILLIAMS, Massachusetts Institute of Technology, and others for the project SQUID, Princeton, N. J. Available in July, 1961.**

Of primary interest to chemical and mechanical engineers and to chemists and physicists interested in kinetics, this timely translation offers a detailed mathematical discussion of the consequences of applying simple thermal combustion theory and simplified (first order) kinetics to over-all combustion problems. This material is not available in comparable detail in any other English source.

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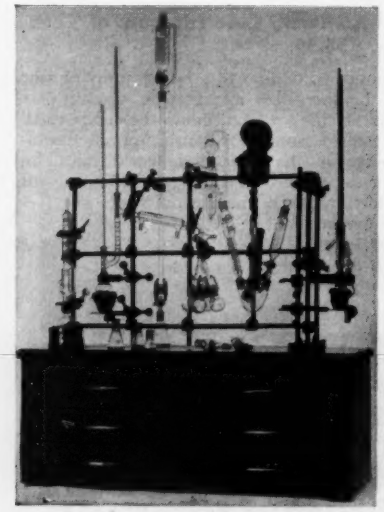

# BOOK REVIEWS

Crabtree effects, in ascites tumors and hela cells. This chapter and the final chapter by Britton Chance, A digital Computor Representation of Chemical and Spectroscopic Studies on Chemical Control of Ascites Tumor Cell Metabolism, conclude a thoroughly interesting symposium.

This book represents a considerable effort from many biochemists. It is a stimulating tribute to Jesse Greenstein. It is the type of symposium that should be available in many areas of investigation to biochemists and deserves their support.

DAVID G. CORNWELL
*Ohio State University*
*Columbus*

### An Introduction to the Chemistry of Heterocyclic Compounds

*R. M. Acheson*, Queen's College, University of Oxford, England. Interscience Publishers, Inc., New York, 1960. xiv + 342 pp. Many figs. 16 × 23.5 cm. $5.

It might be thought, perhaps, that a field as vast as modern heterocyclic chemistry can hardly be surveyed adequately in the space of 342 pages without at least some appearance of superficiality. Here, however, this pitfall has been deftly avoided. In this book Dr. Acheson has succeeded admirably in providing a concise yet highly informative introduction to the chemistry of the fundamental heterocyclic systems without seriously sacrificing important detail. In addition, interesting highlights of many fascinating biochemical areas of the subject are also presented.

Organized according to structures of increasing complexity, from three-membered ring heterocycles through polyheteroatom five- and six-membered ring types, the nine chapters of this book take up each class of compounds logically and systematically. Cardinal features of physical properties and structure, including pertinent data from X-ray, spectral and dipole-moment measurements, are considered first in each section; then the chemical behavior of representative compounds is delineated, along with methods of synthesis and the chemistry of selected substances of natural occurrence and special interest, except alkaloids and carbohydrates. The up-to-date character of the book may be gauged by the fact that, in addition to extensive citation of recent papers and data, modern electronic theory and mechanistic concepts are widely employed, and significant current aspects of the metabolism and biosynthesis of biologically important compounds are described.

For maximum effectiveness the text is illustrated by an unusually large number of clear, well-drawn structural formulas, with bond angles, bond distances, and $\pi$-electron densities marked on those of many of the principal prototypes. A useful general bibliography on each class

*(Continued on page A432)*

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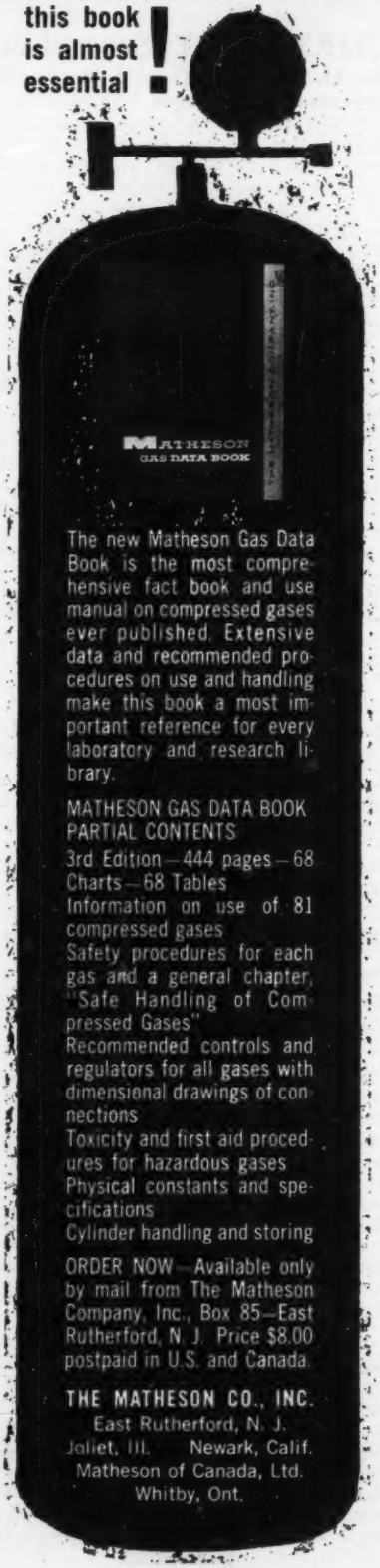


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# Quantitative Organic Microanalysis

**Second Edition**
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**By AL STEYERMARK,** *Microchemical Department, Hoffmann-La Roche Inc., Nutley, New Jersey*

*June 1961, 665 pp., $16.50*

The material included in the first edition has been modified extensively in order to incorporate recent improvements and advances in techniques. In addition, considerable material has been added. All of the methods included have been stringently evaluated for reliability in the hands of many different chemists. The book provides not only these carefully selected methods but also extensive tables of reference at the end of each chapter.

In preparing this second edition the author has drawn upon his broad experience in more than twenty years of performing and directing microanalytical determinations. He has also incorporated the latest recommendations of the American Chemical Society, American Society for Testing Materials, Association of Official Agricultural Chemists, and the International Union of Pure and Applied Chemistry. The author is Chairman of the committees concerned in three of these organizations, and a member of the committee in the fourth.

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**Calculations**
**AUTHOR INDEX—SUBJECT INDEX.**


# Physical Methods in Chemical Analysis

***Edited by* WALTER G. BERL**
*Applied Physics Laboratory, The Johns Hopkins University*

**VOLUME 1** **Second Edition, Revised**

*1960, 686 pp., $19.00*

***Review of first edition:***
"The reader is impressed with the care and thought put into this book to make it helpful to a wide cross section of scientists. It should be available to the experimentalists in the several physical science fields." —*Review of Scientific Instruments*

**VOLUME 2** **Second Edition, Revised**

*1961, in preparation*

***Review of first edition:***
". . . it would not be proper to close this review without saying that analytical chemists owe a considerable debt to the editor, authors and publishers for these two exceedingly valuable volumes." —*The Chemical Age*

**VOLUME 3** *1956, 652 pp., $15.00*

"The volume is a valuable addition to the literature and will be appreciated, not only by analytical chemists, but by all scientists who use new techniques in their research." —*Science*

**VOLUME 4** *July 1961, about 475 pp.*


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AUTHOR INDEX—SUBJECT INDEX.



**ACADEMIC PRESS** *New York and London*

**111 Fifth Avenue, New York 3, New York** **17 Old Queen Street, London, S.W.1**

of compounds discussed is appended to each chapter, and specific references are given to the more recent papers consulted, including some that appeared as late as 1959. A complete compound index and a separate subject index are also included.

Since, as the author observes, "heterocyclic chemistry at the moment accounts for about 26% of the organic papers published," it is indeed unfortunate that the time which is spent on the subject "is proportionately too little in most [undergraduate] teaching schools." It is mainly to help meet this need that this book was written. The sheer mass of material, both classical and contemporary, which exists in the field, easily confuses and overwhelms even the better student, but here at least is a practical and up-to-date guide to the subject that already has sifted out for him the important properties, reactions and methods of synthesis of the major types of heterocyclic compounds.

In this country the principal use for this book will probably be as a supplementary text or reading reference for advanced undergraduate or graduate courses related to heterocyclic chemistry. On the other hand, because of its excellent coverage of recent developments in the field, and its modest price, the book will undoubtedly have a much wider appeal as well.

ALBERT W. BURGSTAHLER
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**Gmelins Handbuch der Anorganischen Chemie. 8 Auflage. System Nummer 15, Silicium, Teil B**

Edited by the Gmelin Institute under the direction of *E. H. B. Pietsch.* 8th edition. Verlag Chemie, GMBH., Weinheim, Bergstrasse, 1959. 923 pp. Figs. and tables. 17.5 × 23.5 cm. Paperbound. $135.50.

The magnitude of the literature on silicon chemistry is evidenced by the size of this volume. This book deals only with elemental silicon and those inorganic silicon compounds which, according to the Gmelin classification, are grouped with silicon.

Over one quarter of the volume concerns itself with the properties of elemental silicon. There is an appendix bringing up to date the literature on the preparation of this element and its use as a semiconductor.

A thorough survey is made of the literature on $SiO_2$. There are 376 pages dealing with such topics as the crystallographic, optical, electrical and solid state properties of $SiO_2$.

The derivatives of this element that tend to polymerize, such as siloxanes, silanols, and siloxenes, are discussed. The industrial importance of silicon carbide accounts for a large section on the silicon-carbon compounds. The preparation and behavior of the glass electrode in aqueous and, to a more limited extent, in non-aqueous media is described exhaustively in the final chapter of this supplement.

This exhaustive study should prove of unlimited value to chemists and physicists alike, especially those interested in semiconductors.

THEODORE R. WILLIAMS
*College of Wooster*
*Wooster, Ohio*

**Nucleic Acid Outlines. Volume I**

*Van R. Potter*, University of Wisconsin, Madison. Burgess Publishing Co., Minneapolis, Minnesota, 1960. vii + 292 pp. Figs. and tables. 14.5 × 22 cm. $5.

The nucleic acid field is so broad, the interrelationships of various aspects so complex, that adequate coverage of the subject has been available only in a comprehensive series of treatises too complicated and too expensive for general classroom use. The absence of a concise, unified presentation of the fundamental information of the entire field has been a serious handicap to those of us who attempt to teach the subject to graduate students with a variety of scientific backgrounds.

The book under review can satisfy only part of the need for a suitable text. It is limited in scope to the treatment of the chemical structures and the metabolic transformations of the nucleic acids, their components and the nucleotide coenzymes. Most conspicuously absent is a discussion of the biological roles of the nucleic acids. This deficiency is apparently to be remedied in the near future

(*Continued on page A434*)

# WILEY — BOOKS

## PHYSICAL CHEMISTRY OF MACROMOLECULES

By Charles Tanford, Duke University. Treats, in turn, the major areas of physical chemistry: molecular structure, molecular statistics, thermodynamics, transport processes, electrostatics, and kinetics. A summary of the fundamental theory is included in each of the areas presented, and it is then shown how the theory may be modified or extended in order to become applicable to molecules of very high molecular weight. In each case, the development is sufficiently rigorous so that the student clearly sees the assumptions which are made, the basis on which he may judge the applicability of any particular technique or theoretical equation to his particular problem.

Illustrated by copious examples from the literature, the book also presents a secondary theme. This is the development of an increasingly detailed knowledge of the structure and behavior of the individual macromolecules.

*1961. Approx. 752 pages. Prob. $15.00*

## TRANSACTIONS OF THE SYMPOSIUM ON ELECTRODE PROCESSES

Edited by Ernest Yeager, Western Reserve University. Includes all the papers presented at an international symposium sponsored by The Electrochemical Society, Inc., and the U. S. Air Force Office of Scientific Research which was held in Philadelphia in May, 1959. While virtually all phases of fundamental investigations of electrode processes are covered, emphasis has been placed on new research developments and, more specifically, on hydrogen discharge kinetics, electrodeposition and dissolution of metals, the electrical double layer, adsorption phenomena, and the kinetics of fast electrode processes. In addition to the important papers offered, the book also contains the extensive and extremely analytical discussion that revolved around the papers. *1961. Approx. 484 pages. Prob. $20.00.*

## MINERALS FOR THE CHEMICAL AND ALLIED INDUSTRIES *Second Edition*

By Sydney J. Johnstone, Technical Consultant. 1961. In press.

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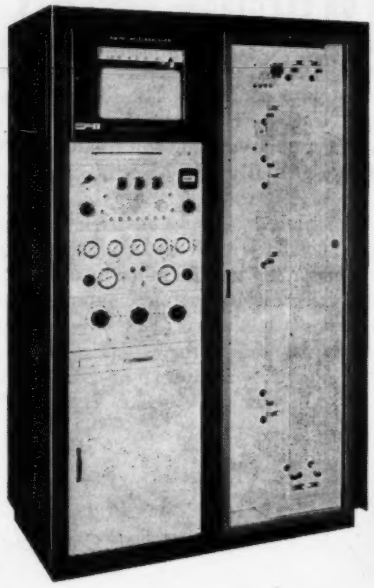

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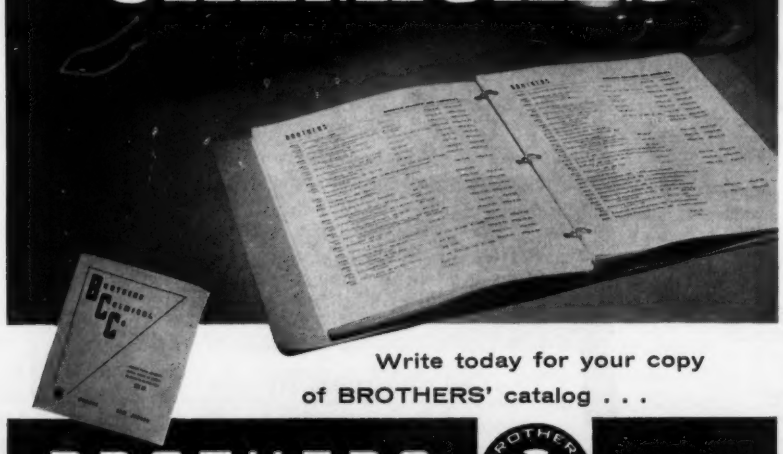

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# BOOK REVIEWS

with the planned appearance of a companion volume by the same author which will treat nucleic acid function and related topics. There is every reason to assume that the second volume will be of the same high caliber as the first. The combination of the two volumes should serve admirably in any general course on the biochemistry of the nucleic acids.

Many a lecturer, however, will find this first volume to be sufficient for his purposes, providing a foundation upon which to build structures of his own choice. The book is an excellent, ready source of up-to-date basic information of nucleic acid chemistry and metabolism. As befits the title of the book, the material is given in semi-outline form. The presentation is concise and surprisingly complete, yet it is unusually lucid. The discussion of experimental methods is brief or lacking, but references to the original literature are numerous. Factual material is emphasized, but present areas of uncertainty are clearly indicated and the opinions and the philosophy of the author are refreshingly apparent.

The major defect of the book, considering it as an attempt to provide a broad, minimal background of the chemistry and metabolism of the nucleic acids, is the absence of information on the chemical synthesis of mono and oligonucleotides and on the physical properties of the polynucleotides, natural and synthetic. This deficiency is recognized by the author, and, it is to be hoped, may be removed in a future edition.


JAMES L. FAIRLEY
*Michigan State University*
*East Lansing*


### Substitution at Elements Other Than Carbon

*C. K. Ingold*, University College, London. The Weizmann Science Press of Israel, Jerusalem, 1959. 52 pp. 6 figs. 5 tables. 15 × 22 cm. $1.75. (Distributed by the Weizmann Institute of Science, Rehovot)

This book contains two chapters which summarize 4 lectures delivered by C. K. Ingold on the occasion of the 5th Weizmann Memorial Lecture Series, May, 1958. The first is entitled "Nucleophilic Substitution at Octahedral Metal Atoms, in Particular Cobalt" and the second "Electrophilic Substitution at Nitrogen and Oxygen."

The discussion in Chapter I is based on the premise that the more complicated mechanisms of substitution of ligands of complex ions are best understood when compared with the simpler nucleophilic substitutions at carbon. The lecturer developed an interpretation based on available rate and stereo chemical data which he characterizes thus: "I do not dare to hope that the interpretations I have suggested are correct in their entirety. But I do believe them sufficiently to think they are more likely to be modified than scrapped."


*(Continued on page A438)*

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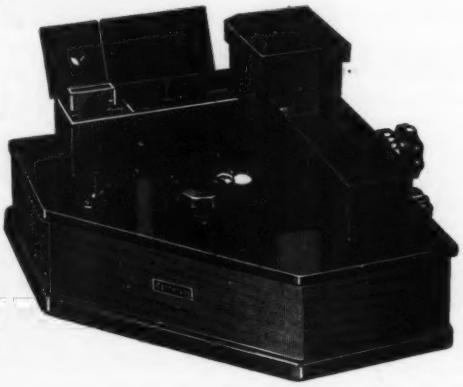

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# BOOK REVIEWS

In Chapter II the lecturer dealt with nitration and nitrosation in his usual thorough manner. First he indicated the possible species that could be the reagent and showed the kinetic form that the rate equation should have for each. Comparison of the experimental results with the kinetic forms expected gave strong indications as to the nature of the reactive species under different conditions. This chapter gives a convenient summary of the mechanism of nitration and nitrosation.

This short book is worthy of inclusion in a chemists' personal library.


JOHN D. REINHEIMER
*College of Wooster*
*Wooster, Ohio*


### Radioisotope Techniques

*Ralph T. Overman*, Oak Ridge Institute of Nuclear Studies, and *Herbert M. Clark*, Rensselaer Polytechnic Institute, Troy, New York. McGraw-Hill Book Company, Inc., 1960. xiv + 476 pp. Figs. and tables. 16 × 23.5 cm. $10.

This book is the outgrowth of courses given over the past years at ORINS and Rensselaer Polytechnic Institute, places where instruction in the use of radioisotopes is more varied and where facilities are somewhat more extensive than at most colleges and universities.

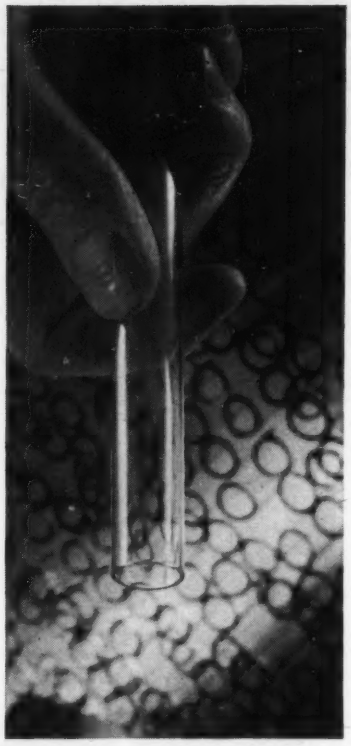
The first chapter treats in 24 pages "Nuclear Radiations and Their Interactions with Matter," topics which occupy at least a third of a one-semester course given by the reviewer. The second chapter encompasses discussion, with illustrations, of the common detectors of individual events as well as the associated instrumentation such as discriminators and differential pulse height analyzers. No discussion of electronic circuitry is included. The same chapter very briefly mentions chemical and photographic dosimeters. At the end of this and of each subsequent chapter, several experiments are described incorporating and supplementing the textual material of that chapter.

Chapter 3, on errors in radioactivity measurements, is a mature general errors treatment from which the authors lead to the application of radioactive disintegration. Chapter 4 deals with practice of radiological safety. The next three chapters deal, respectively, with techniques of preparation of radioactive sources, laboratory characterization of radiation, and standardization of radioactive sources and calibration of detectors. Rather late in the reviewer's opinion comes the treatment of radioactive decay and growth kinetics in Chapter 8. This is the first text to present the counting procedure for determination of relatively short half lives of about one minute.

Chapter 9, on radiochemical separation methods, seems to be in exile, quite removed from the earlier chapters on techniques of handling of radioisotopes.


*(Continued on page A438)*





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# BOOK REVIEWS

The last chapter appropriately is on applications of radioisotopes to the solution of many problems some of which are uniquely solved by use of tracers. After each chapter and especially after Chapter 10 are numerous, usually non-critical, references to other texts, reference books and the journals.

A set of 36 problems appears after the last chapter. They span the material covered in the text but are less challenging and less numerous than would be desired to stimulate mature thinking. Of the 11 appendixes supplied, the most useful was the list of thermal neutron activation cross sections together with isotope abundances and half lives of activities produced.

After a semester's experience in the use of this text in a radiochemistry course, the reviewer is all the more convinced that textbooks should emphasize principles. Specialized setups for radioactive measurements are so numerous and so much in a state of flux that any catalog of them rapidly becomes archaic. The mood of "Radioisotope Techniques" is more that of a cook book than that for stimulation of student thinking. Since the principles are superficially discussed and are intermeshed with the laboratory instructions, one experiences difficulty in the use of the text as a reference book for other than advice on procedures. Equations are presented as formulas rather than as relationships linked to fundamental concepts.

It is expected that this book will be used principally by instructors in choosing appropriate experiments for laboratory sessions.

JAMES E. STURM
*Lehigh University*
*Bethlehem, Pennsylvania*

**Advances in Organic Chemistry: Methods and Results. Volumes 1 and 2**

Edited by *Ralph A. Raphael*, University of Glasgow, Scotland, *E. C. Taylor*, Princeton University, Princeton, New Jersey, and *Hans Wynberg*, Rijksuniversiteit, Leiden, Netherlands. Interscience Publishers, Inc., New York, 1960. Volume 1: ix + 387 pp. Figs. and tables. 16 × 23.5 cm. $12. Volume 2: vii + 504 pp. Figs. and tables. 16 × 23.5 cm. $15.

These are the first two volumes of an intended series. The stated objective is to present "articles providing a critical appraisal and evaluation of new aspects ripe for further development, and of novel extensions to well-established methods."

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The general character of these two volumes is much like *Chemical Reviews*. The several articles differ in type of material, in emphasis and in style just as do contributions to that journal. A point of difference is that these "*Advances*," no doubt owing to a more aggressive editorial approach, generally deal with topics more central to the main stream of organic chemistry.

Some of the articles, those which adhere most closely to the aim of the series, sketch a balanced picture of a method (physical or organic chemical) of great current utility. Others go into exhaustive, even painful detail on synthetic methods of narrower scope. All but one of the chapters on synthesis give a few representative experimental procedures, a laudable feature. A few give extensive tables reminiscent of "Organic Reactions." One article presents the detailed chemistry of an alkaloid (muscarine), and seems out of place.

(*Continued on page A440*)

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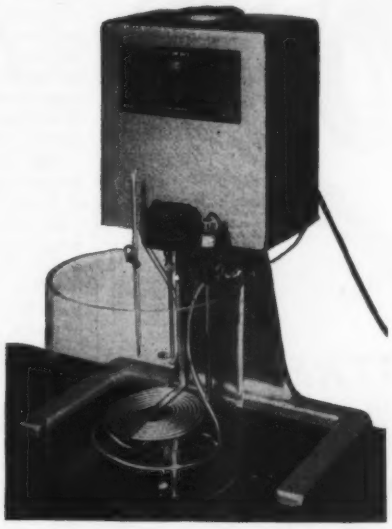

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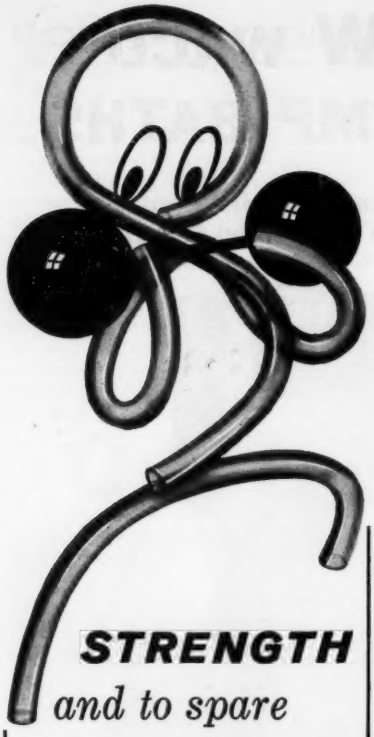

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# BOOK REVIEWS

These volumes are addressed to researchers who contemplate use of the methods discussed. Little attention has been given to the less intensive reader (e.g., the graduate student studying for cumulative exams) who seeks an authoritative summary of the highlights, rather than a thorough treatment. A few chapters are exceptions to this statement, and for a few topics (such as nuclear magnetic resonance) abbreviation would not be consistent with fidelity to the subject. Readers of all types would be served by a two or three page introduction, where feasible, covering the salient points. It is hoped that articles in future volumes will contain such sections.

The books are sturdily constructed and attractively printed, with an abundance of lucid structural formulas.

In considering whether to buy these volumes, one must note that several articles deal with subjects ably presented in other current reviews or books. Notwithstanding, acquisition is essential for libraries of institutions with a serious interest in organic research. Purchase by individual organikers is also easily justified.


JOSEPH F. BUNNETT
*Institut für organische Chemie der Universität München (regularly at Brown University, Providence, Rhode Island)*


### Style Guide for Chemists

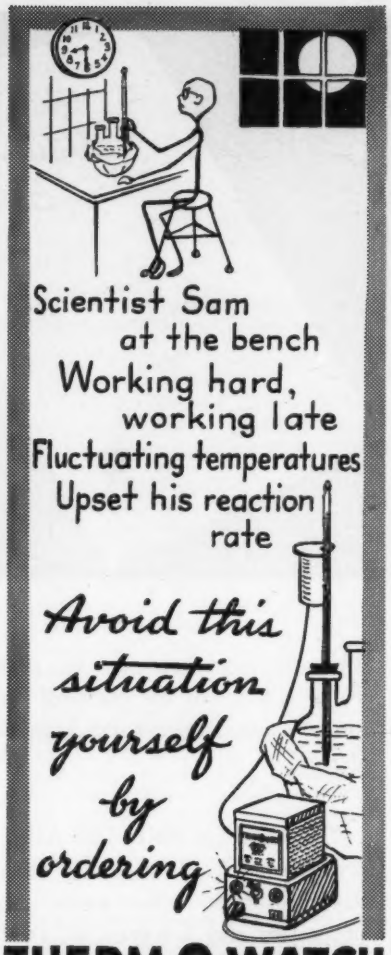
*Louis F. Fieser*, and *Mary Fieser*, both of Harvard University. Reinhold Publishing Corp. New York, N. Y. 1960. vi + 116 pp. 16 × 23.5 cm. $2.95.

*"We chemists are not concerned with creative writing, nor do we aspire to any real artistry. Our objective is to make our technical writing clear, understandable, forceful and interesting."* (Fieser and Fieser, "Style Guide for Chemists," p. 51.)

The purpose of scientific writing is the communication to others of ideas and experience. Any feature of such writing not directed to this purpose must be avoided by those who wish to write well. A brief but very valuable guide to effective writing in the chemical field has now been provided by the Fiesers; the principles set forth are surely applicable to scientific writing in all fields, and do not differ from those governing effective writing in any field.

Good writers are made, not born, and Louis Fieser has taken pains not only in this book but elsewhere to give examples from his own early papers of poor and ineffective writing. He is now universally regarded as one of the most competent writers now practicing in the chemical field, and we can all profit by the experience and knowledge he and his able collaborator, Mary Fieser, have acquired in the process of becoming good writers.

*(Continued on page A442)*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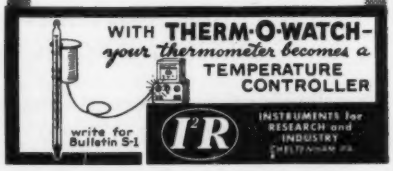

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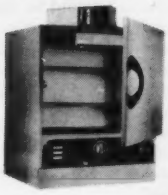

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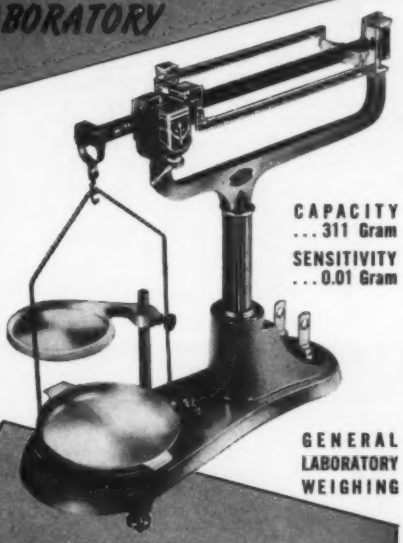

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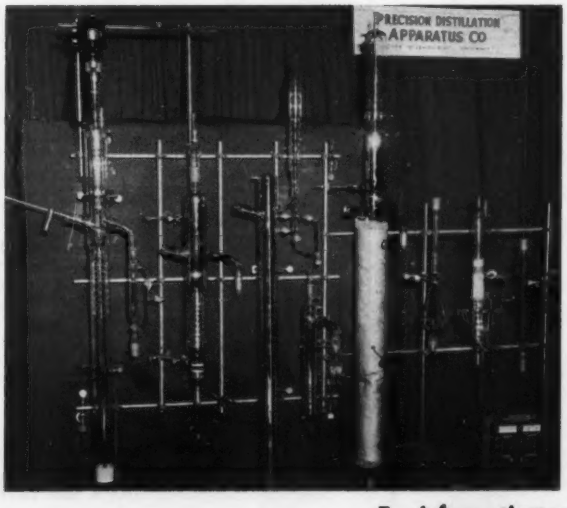


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The book is in essence a "how to" rather than a "why" book, and the Fiesers are quick to point out that the principles of usage are those set forth by such authorities as H. W. Fowler ("Modern English Usage," Oxford University Press, 1926, 1958), H. W. Fowler and F. G. Fowler ("The King's English," Oxford, 1926, 1954), W. Strunk, Jr. and E. B. White ("The Elements of Style," Macmillan, 1959) and others. To these I would add Sir Earnest Gowers ("Plain Words, Their ABC," Alfred A. Knopf, 1957).

Appropriately, the book begins with a discussion of concise writing, and proceeds then to a treatment of a number of grammatical points which give much trouble. Word choice is treated in an important chapter, and a short but pithy chapter dealing with style, the burden of which is that we can do nicely without style, is well worth the attention of us all.

Two chapters not dealing directly with writing, one on pronunciation and one on speaking, are included. The first of these is likely to prove the most controversial part of the book, although the authors quite clearly have no wish to provoke controversy. Our prejudices as to pronunciation are formed early and cherished late, and no realist expects much change in those of us whose habits have been formed. The Fiesers recognize this, and hope their recommendations may be of guidance to those whose prejudices have not yet solidified.

The chapter on speaking is brief, but presents many practical points taken from the experience of one of the acknowledged master teachers of our time.

Editors are perhaps more sensitive than most to the faults the Fiesers' book is designed to correct. Certainly an editor's life would be easier, and what is vastly more important, our chemical literature would be clearer, more concise, more effective and more interesting if those who write, particularly those younger men just embarking on productive scientific careers, would "read, ponder and inwardly digest" the Fiesers' fine little book.

MARSHALL GATES
*University of Rochester*
*Rochester, New York*

**Comparative Biochemistry. Volume 1, Sources of Free Energy**

Edited by *Marcel Florkin*, University of Liége, Belgium, and *Howard S. Mason*, University of Oregon Medical School, Portland, Oregon. Academic Press, Inc., New York, 1960. xxv + 590 pp. Figs. and tables. 16 × 23 cm. $18.

This book is Volume 1 of a four-volume "Comprehensive Treatise" on comparative biochemistry, which is being edited by Florkin and Mason to fill the need, as they say, for a "sound, critical and provocative summary of present knowledge in the field." Volume 2, "Free Energy and Biological Function" appeared some time ago; the present volume deals with "Sources of Free Energy."

Besides a guide to nomenclature and classification of organisms, and an Introduction by the Editors, Volume 1 includes chapters on Thermodynamics of Living Systems by H. Eyring, R. P. Boyce and J. D. Spikes; Comparative Mechanisms for Fatty Acid Oxidation by P. K. Stumpf and G. A. Barber; Phosphoric Acid Anhydrides and Other Energy-Rich Compounds by F. M. Huennekens and H. R. Whiteley; Onium Compounds and Their Biological Significance by G. L. Cantoni; Phototropism and Photoaxis by K. V. Thimann and G. M. Curry; The Distribution and Evolution of Visual Systems by G. Wald; Aerobic and Anaerobic Reactions of Inorganic Substances by C. Fromageot and J. C. Senez; Comparative Biochemistry of Glycolysis by E. Bueding and E. Farber; Comparative Biochemistry of Electron Transport by E. E. Conn; and Utilization of Thermal Energy by Living Organisms by M. B. Allen.

The individual contributions range from poor to extremely fine, and the general level is very good indeed. The section by Eyring is far below his usual standard; he and his collaborators have attempted to summarize all of thermodynamics and the theory of absolute reaction rates in 60 pages and have succeeded only in creating confusion. On the other hand, Wald's article on visual systems is a pure delight, admirable for its ideas and sprightly in its style. Cantoni's paper on onium compounds is a splendid example of a solid piece of work; it gives all the information one could

(*Continued on page A444*)

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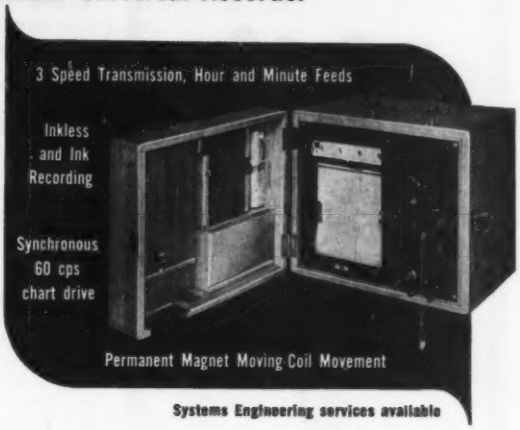
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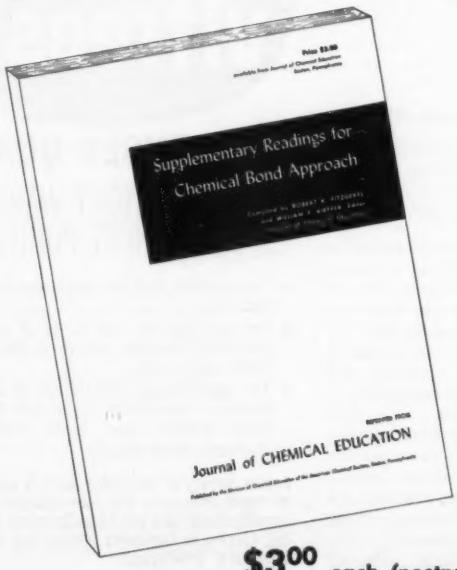


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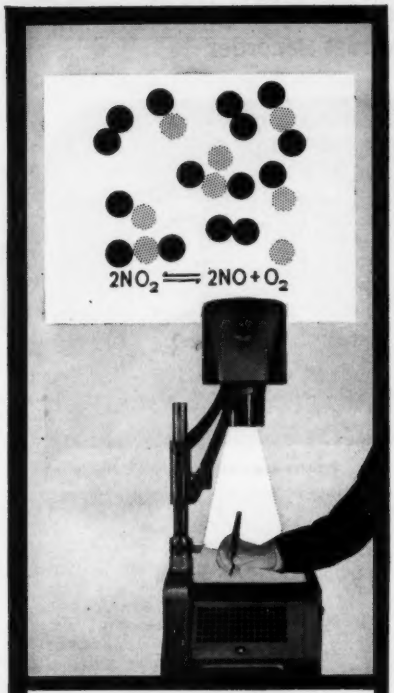


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# BOOK REVIEWS

possibly ask, documents it thoroughly with references, and discusses all aspects of the subject quite soundly.

There is not space here to discuss each of the other papers individually. They vary widely, however, in the amount of detail which they give, so that some of the papers (Bueding and Farber, Allen) would be worthwhile reading as a brief introduction for those not familar with the field, whereas others (Huennekens and Whiteley) could serve as critical summaries, of interest even to specialists.

Despite the generally high quality, the volume has many flaws which are attributable to deficient editing. It seems to this reviewer that the editors should take the responsibility not only for soliciting contributions, but also for making sure that the papers are written clearly and in good English, and for seeing that everything necessary for easy comprehension is included. For example, the guide to nomenclature and classification—an excellent idea—fails to include many of the taxonomic groups to which repeated reference is made by the various authors; if the scheme were just a little more detailed it would be several times as useful. The excellent article by Cantoni contains long tables of structural formulas of onium compounds, without the names, and a text full of names without formulas.

These instances could be multiplied many times; the reviewer did not find a single paper which would not have been improved by careful editing.

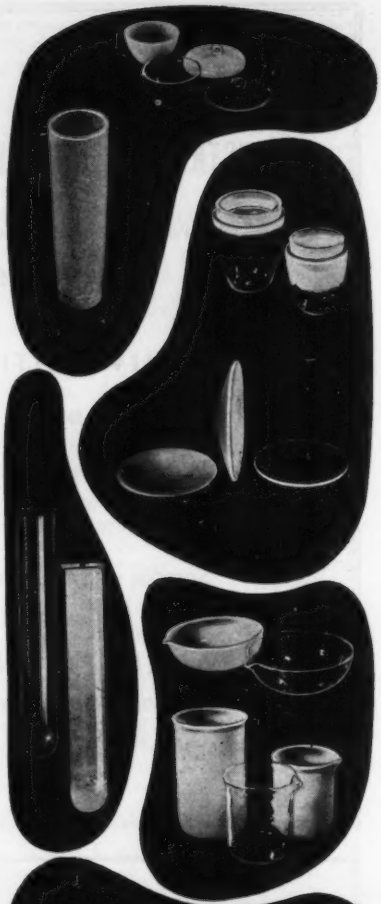
PETER OESPER
*Hahnemann Medical College*
*Philadelphia, Pennsylvania*

**Organic Syntheses. Volume 40**

Edited by *Melvin S. Newman*, Ohio State University, Columbus. John Wiley & Sons, Inc., New York, 1960. vii + 114 pages. 15.5 × 23.5 cm. $4.

This addition to the series maintains the high standards set by previous volumes. The volume contains 39 syntheses, the less familiar of which are a benzyne synthesis and a free radical coupling of an aliphatic radical. The products run the gamut of organic compounds, from aliphatic and aromatic hydrocarbons to heterocyclics to several ferrocene derivatives. The usual care in listing dangers and precautions has been taken. The notes on the reactions are extensive, even to the point of naming the type of stirring motor required for efficient stirring. A new feature, point 4 under several of the syntheses, is the listing of uses of the products. The reviewer finds this additional information valuable. While most of the syntheses were submitted by American chemists, a few came from overseas.

JOHN D. REINHEIMER
*College of Wooster*
*Wooster, Ohio*



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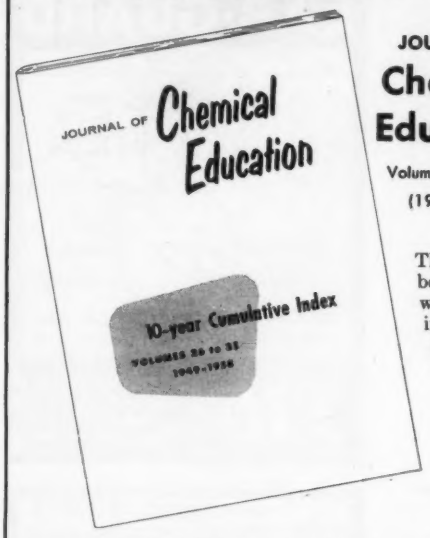


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This index has been prepared with the special interests of the J.-Chem.-Ed. user in mind. Not only are the conventional entries made by author, title, and inverted title, but many suggestive subject listings have been used. For example, reference to an article entitled "Infrared Spectra of Chemisorbed Molecules" can be found under "acetylene," one of the compounds discussed. Preparation of the index involved hundreds of hours of careful checking not only of annual indexes, but the original articles for subject content.

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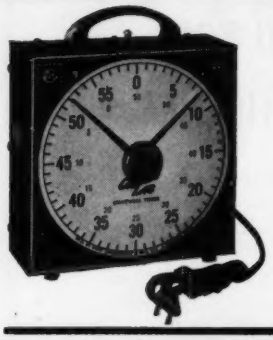

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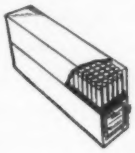

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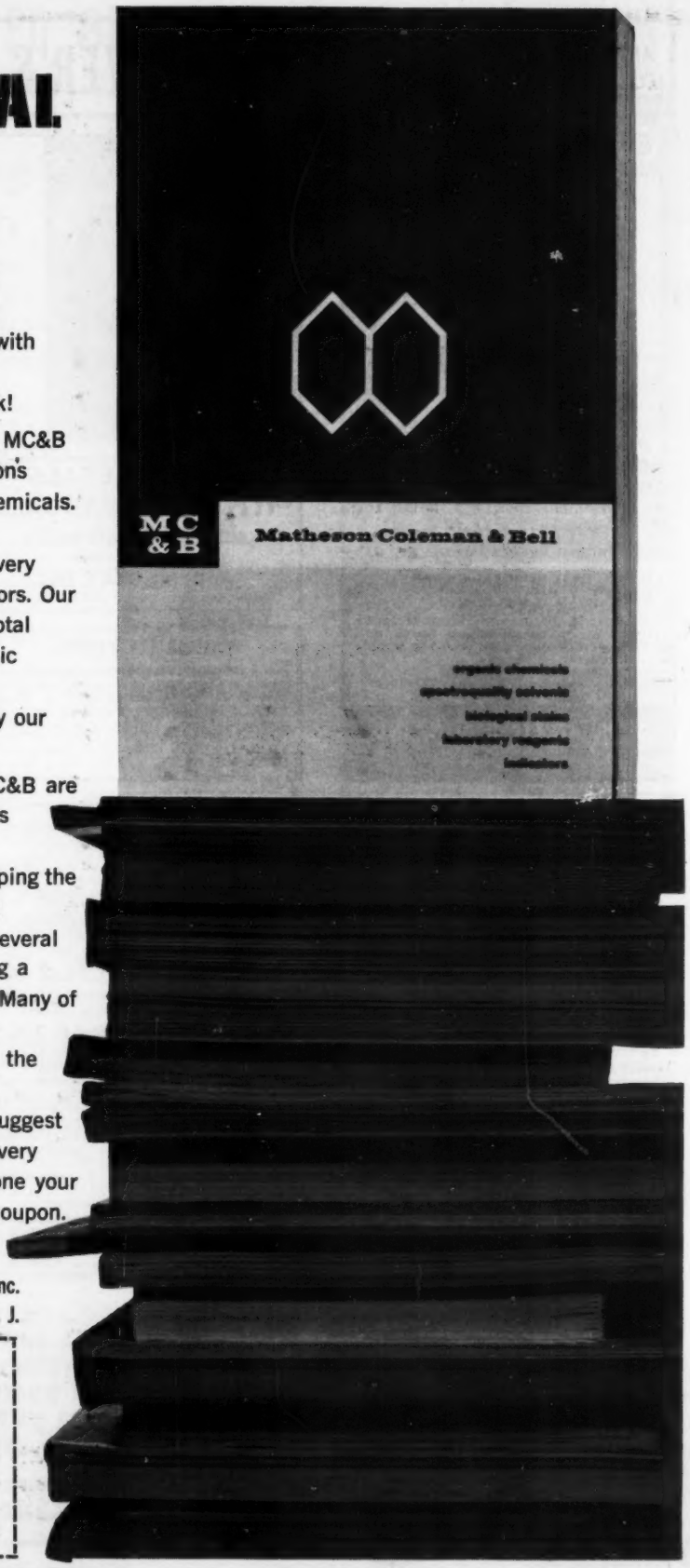


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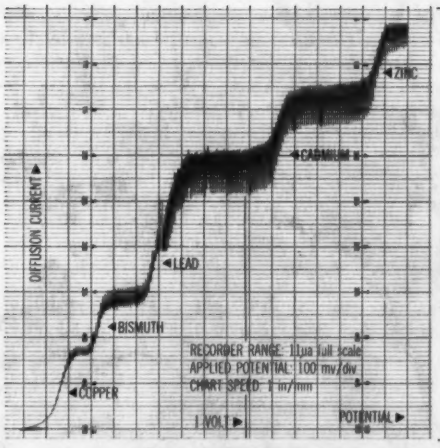


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